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DRAFT WORK PLAN FOR THE INTERIM RESPONSE ACTIVITY OF EVALUATING WILD GAME TAKEN FROM THE TITTABAWASSEE RIVER FLOODPLAIN

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Definitions and Acronyms

AhR	Aryl Hydrocarbon Receptor
DQOs	Data Quality Objectives
FSP	Field Sampling Plan
MDCH	Michigan Department of Community Health
MDEQ	Michigan Department of Environmental Quality
MDNR	Michigan Department of Natural Resources
PCBs	Polychlorinated Biphenyls
PCDDs	Polychlorinated Dibenzo-*p*-Dioxins
PCDFs	Polychlorinated Dibenzofurans
QAPP	Quality Assurance Project Plan
RI	Remedial Investigation
S-HASP	Site Specific Health and Safety Plan
SOP	Standard Operating Procedure
TEFs	Toxic Equivalency Factors
TEQs	TCDD equivalents
TCDD	2,3,7,8-Tetrachlorodibenzo-*p*-dioxin
USFWS	United States Fish and Wildlife Services
WGS	Wild Game Sampling
WHO	World Health Organization

1.0 INTRODUCTION

The Tittabawassee River study area, hereafter referred to as the “Site”, includes sediments and floodplain soils for approximately 23 miles of the Tittabawassee River downstream of Midland, Michigan. Specifically, the Site includes the upstream boundary of The Dow Chemical Company to the confluence of the Tittabawassee and Shiawassee Rivers downstream of Greenpoint Island, as defined in the Hazardous Waste Management Facility Operating License, which was issued on June 12, 2003 by Michigan Department of Environmental Quality (MDEQ) to The Dow Chemical Company (Dow).

Previous documents have reported concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in the sediments, floodplain soils, and fish of the Tittabawassee River that exceed some state generic criteria (Taylor et al., 2002, Hilsherova et al., 2003, MDEQ, 2003). As outlined in the Operating License, specific interim response activities (IRAs) have to be undertaken. An IRA is a short-term action that is taken to control or understand ongoing risks while the site characterization is underway or a final remedy is selected. One of the IRA items identified in Dow’s Scope of Work (submitted to MDEQ on August 12, 2003) and brought up during Community Advisory Panel (CAP) meetings is the potential for human exposure to PCDDs and PCDFs from wild game harvested within the Tittabawassee River floodplain and the potential risks associated with the consumption of those game species. To date, no information exists for PCDDs and/or PCDFs in wild game species that inhabit the Tittabawassee River floodplain. The purpose of this study is to determine if wild game taken from the Tittabawassee River floodplain represent a relevant human exposure pathway to PCDDs and PCDFs. Following a September 18, 2003 meeting between MDEQ, U.S. Fish and Wildlife Service (USFWS), Michigan Department of Natural Resources (MDNR) Wildlife Division, Dow, and ENTRIX, a decision was made to conduct a wild game sampling study in order to address community concerns. The timeline for this study was targeted for the Fall of 2003. It was decided that ENTRIX would prepare the wild game sampling plan for further review by MDEQ, MDCH, MDNR, and USFWS.

1.1 Purpose

As specified in the “Work Scope for the Interim Response Activity of Evaluating Wild Game Taken from the Tittabawassee River Floodplain” submitted by Dow and approved by MDEQ on October 21, 2003, a Draft Wild Game Sampling (WGS) Work Plan for the Tittabawassee River near Midland, Michigan was developed, hereafter referred to as the WGS Work Plan (Carrington, 2003; MDEQ, 2003b). The overall purpose of this WGS work plan is to determine if wild game taken from the Tittabawassee River floodplain represent a relevant human exposure pathway to PCDDs and PCDFs or not. Thus, this WGS Work Plan will be limited in focus to evaluate whether there are differences in concentrations of PCDDs and PCDFs between populations of selected wild game species inhabiting the floodplain of the Tittabawassee River downstream of the Dow property in Midland as compared to the same species collected from a reference area.

1.2 Rationale

Due to the results of previous investigations demonstrating that some concentrations of PCDDs and PCDFs in the Tittabawassee River floodplain soils downstream of Midland are greater than those from reference locations (MDEQ, 2002, 2003; Hilsherova et al., 2003), questions have been raised regarding human consumption of wild game that reside and/or forage within the Tittabawassee River floodplain. Currently, there is no information on the presence or concentration of PCDDs and PCDFs in wild game species that reside within the Tittabawassee River floodplain downstream of Midland, Michigan or from other locations that could be used as reference areas. A search of the published scientific literature on this question failed to find any available information on concentrations of PCDDs and PCDFs in wild game that would be applicable to this Site. As a result, this WGS Work Plan is designed to provide a survey of tissue residue concentrations in wild game animals, such as white-tailed deer, wild turkey, and rabbits, that are potentially exposed to PCDDs and PCDFs in the Tittabawassee River floodplain soils. The results from this field study will be used to:

- inform the public and other interested stakeholders of concentrations of PCDD/PCDF congeners and total TEQs (based on PCDDs and PCDFs as described in section 1.4) in selected tissues of wild game collected from the Tittabawassee River floodplain downstream of Midland,
- determine how those tissue residue concentrations compare to similar wild game samples collected from a reference area,
- determine how those tissue residue concentrations compare to other food items (e.g., literature review of recent market basket results),
- determine if wild game taken from the Tittabawassee River Floodplain represents a relevant human exposure pathway to PCDDs and PCDFs, and
- evaluate the need for further study or risk mitigation for the protection of human health and welfare for consumers of wild game collected from the Tittabawassee River floodplain downstream of Midland.

1.3 Data Quality Objectives

A set of data quality objectives (DQOs) has been developed in accordance with the EPA DQO process (EPA 1997). The DQOs for the WGS Work Plan are summarized in the following steps:

<u>DQO Step 1: Problem Formulation</u>: Concern has been raised that people that hunt and consume wild game that reside and/or forage within the Tittabawassee River floodplain downstream of Midland may be exposed to PCDD/PCDF via this pathway. The problem can be briefly summarized in the form of a question to be answered with site-related data:

Are concentrations of TEQs in wild game collected from the Tittabawassee River floodplain downstream of Midland significantly greater than concentrations of TEQs in wild game collected at an upstream reference location?

This decision is described in more detail as part of the Decision Procedure Document (Appendix A) (also see DQO Steps 5, 6, and 7 below). Specifically, this document describes how this decision fits into a decision tree-based approach. In addition, this document provides discussion of statistical tests, statistical power, and other pertinent factors (e.g., the reasonable suitability of the reference areas for background comparisons, etc.).

<u>DQO Step 2: Decisions to be Made.</u> Decisions to be made that are relevant to determine whether TEQs pose an unacceptable risk(s) to humans are outlined below:

Decision 1. *What is the potential incremental risk to humans caused by the concentrations of TEQs in wild game taken from the Tittabawassee River floodplain if these concentrations are greater than concentrations observed in wild game taken from the reference location?*

Decision 2. *Do concentrations of TEQs in wild game pose an unacceptable risk to people that hunt and consume wild game within the Tittabawassee River floodplain downstream of Midland?*

This decision is described in more detail as part of the Decision Procedure Document. Factors to be considered in this evaluation include, yet are not limited to, the potential incremental risk relative to background, comparison to concentrations of TEQs from other sources of protein that have been measured as part of recent market basket surveys, exposure factor assumptions relative to wild game consumption, and uncertainties. Probabilistic risk assessment, incorporating probability distribution function data on key exposure parameters, will be used to assess theoretical increases in incremental risk due to consumption of wild game.

DQO Step 3: Information Needed to Make the Decision. The existing information from the Tittabawassee River and its floodplain was reviewed and subsequently judged to be insufficient to determine whether PCDD/PCDF concentrations in wildlife exceed concentrations that could produce adverse human health effects. As presented in the following text, the species selected for this evaluation have characteristics that warranted their inclusion in this investigation. In particular, they are important wild game species that are actively hunted within the study area and are a source of protein for individuals that consume the wild game.

The three species selected for this investigation are the white-tailed deer (*Odocoileus virginianus*), wild turkey (*Meleagris gallopavo*) and cottontail rabbit (*Sylvilagus floridanus*). These species were selected due to their presence within the Tittabawassee River floodplain and the fact that they are wild game species that are hunted within the floodplain. Wild turkey and cottontail rabbits are herbivores that are resident species in the region that make them a good indicator of conditions within the floodplain. White-tailed deer are also herbivores and are also resident species that inhabit the floodplain. Deer are a particularly important game species because they are heavily hunted and can be a source of protein for some individuals.

DQO Step 4: Boundaries of the Study. The spatial boundaries of this study include an area from approximately 23 miles of the Tittabawassee River downstream of Midland, Michigan also referenced in this document as the "Site". Specifically, there are three study areas located within the 100-y floodplain including two downstream sites and one reference site upstream of Midland area. The temporal boundaries consist of comparable time frames for collecting samples from the upstream reference area as well as the two downstream study areas.

DQO Step 5: Decision Rule. The decision to be made is the following:

Are concentrations of TEQs significantly greater in wild game collected downstream of Midland as compared to wildgame collected from an upstream reference location?

Statistical procedures that will be used for comparing significant differences between groups are described in the Decision Procedure Document. Depending on the various outcomes of those results, a decision will be made whether the data are sufficient to conclude whether further evaluation and/or studies are necessary and/or whether a technically valid conclusion can be made.

DQO Step 6: Specify Tolerable Limits on Decision Errors. Specifying limits on decision errors involves defining the possible decision errors and the consequences of making these errors. Typically, this is done by describing the decisions in terms of hypothesis tests or other objective decision criteria and by specifying the hypotheses to be tested using an appropriate statistical model. Limits can also be specified by identifying the decision errors as false-positive and false negative errors. Statements regarding decision error limits will be given for each wild game species within the Decision Procedure Document.

DQO Step 7: Optimize the Design.

The study design has been optimized based in part on discussions with MDEQ and other interested parties and agencies. If analysis shows that the sample size is too small while the variability is too great to reduce the probability of a type II error, then subsequent studies may be designed and implemented to obtain the additional necessary data to answer the questions posed in DQO Steps 1 and 2.

1.4 Polychlorinated Dibenzo-*p*-dioxin (PCDD) and Dibenzofuran (PCDF) Congeners

There are 75 PCDD congeners and 135 PCDF congeners that vary in the degree and position of chlorine substitution. Despite their structural relatedness, each of these congeners has different physico-chemical properties that affect their fate, transport, and bioavailability in the environment. In general, many PCDD and PCDF congeners in the environment are predominantly associated with particulate material, such as sediments, suspended material, and soils.

Of the 210 PCDD and PCDF congeners, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD, also referred to as TCDD) is considered to be the most potent and is the one most studied. For example, the potency of TCDD and related compounds in avian and mammalian wildlife has been well-established in laboratory and field studies (Murray et al., 1979; Gilbertson et al., 1991; Giesy et al., 1994a and 1994b; Ludwig et al.,1996; Tillitt et al., 1996; Powell et al., 1997). Observed effects of TCDD and related chemicals in wildlife and laboratory animals include biochemical adaptive changes such as enzyme induction, developmental deformities, reproductive failure, liver damage, wasting syndrome, and death.

The mechanism of action of TCDD and related compounds at the cellular level is primarily mediated through the aryl hydrocarbon receptor (AhR). Because of this assumed similarity in mechanism of action, concentrations of 17 PCDD and PCDF congeners substituted with chlorines at positions 2, 3, 7, and 8, are routinely converted to TCDD equivalents (TEQs) using the 1998 World Health Organization (WHO) toxic equivalency factors (TEFs), (Table 1-1, Van den Berg et al., 1998) (Equation 1-1).

$$TEQ = \sum\nolimits_{i \to n} [(Congener_i \times TEF_i) + ...(Congener_n \times TEF_n)] \qquad \textbf{(Equation 1-1)}$$

Table 1-1. Mammal, fish, and bird-specific toxic equivalency factors (TEFs) from the World Health Organization (WHO) for the 2,3,7,8-chlorine substituted PCDD and PCDF congeners.

	WHO 1998 TEF Values		
	Mammals/ Humans	**Fish**	**Birds**
Polychlorinated dibenzo-*p*-dioxins			
2,3,7,8-TCDD	1	1	1
1,2,3,7,8-PeCDD	1	1	1
1,2,3,4,7,8-HxCDD	0.1	0.5	0.05
1,2,3,6,7,8-HxCDD	0.1	0.01	0.01
1,2,3,7,8,9-HxCDD	0.1	0.01	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.001	< 0.001
OCDD	0.0001	< 0.0001	0.0001
Polychlorinated dibenzofurans			
2,3,7,8-TCDF	0.1	0.05	1
1,2,3,7,8-PeCDF	0.05	0.05	0.1
2,3,4,7,8-PeCDF	0.5	0.5	1
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
OCDF	0.0001	< 0.0001	0.0001

Source: Van den Berg et al., (1998)

1.5 Outline of General Strategy

To accomplish the study objectives, information will be collected to determine the presence or absence of targeted game species for sampling and determine the current concentrations of PCDDs and PCDFs in selected tissues.

The field studies described in this WGS Work Plan have been designed to maximize the utilizable information gained. The biota to be sampled include white-tailed deer, turkey, and rabbit, which are all species that are generally consumed by the hunting public.

The following is a summary of the general strategy for this WGS Work Plan:

1. Collect wild game samples from the primary study area (i.e., the Tittabawassee River floodplain downstream of Midland) and an upstream reference area,
2. Conduct congener-specific PCDD and PCDF analysis on select tissue samples from wild game animals collected from various locations on the Tittabawassee River floodplain (results to be reported on a wet weight and lipid-adjusted basis),
3. Calculate the concentration of TEQs based on measured concentrations of PCDDs and PCDFs, and
4. Evaluate the data with the Decision Procedure Document.

1.6 Description of Study Area

1.6.1 Overview

This section provides a physical description of the Tittabawassee River encompassing the Site and characterizes the general habitat associated with the Site.

1.6.2 General Characteristics

The Tittabawassee River is located in central Michigan, and begins at the confluence of the Tobacco and Molasses Rivers. As part of the Saginaw River watershed, the Tittabawassee flows from the north through Midland Michigan in a southeastern direction to the confluence with Saginaw River and eventually to Saginaw Bay. The stretch of the river between Midland and the confluence with the Saginaw River is approximately 23 miles. The Tittabawassee drains 6,200 square kilometers of land in the Saginaw River watershed and is one of four tributaries which combined comprise 84% of the total Saginaw River drainage area (MDNR, 1988).

As described earlier, the Tittabawassee River Site, as defined in the Hazardous Waste Management Facility Operating License (issued on June 12, 2003 by Michigan Department of Environmental Quality to The Dow Chemical Company), includes approximately 23 miles of the Tittabawassee River from the upstream boundary of The Dow Chemical Company to the confluence of the Tittabawassee and Shiawassee Rivers downstream of Greenpoint Island. The Site area includes only one dam, which is within the confines of The Dow Chemical Company property. Beyond The Dow Dam, the river is free-flowing to the confluence with the Saginaw River.

1.7 Work Plan Organization

The remainder of this WGS Work Plan is organized into the following sections and appendices as follows:

Section 2.0. Field Sampling Plan (FSP)

This section provides details concerning what chemical, physical, and biological measurements will be made while conducting the studies described.

Section 3.0. Schedule and Reporting

This section provides an overview of the project schedule.

Appendix A. Decision Procedure Document

The Decision Procedure Document describes a decision tree-based approach for determining the conclusions to be drawn from this study. In addition, this document provides discussion of statistical tests, statistical power, and other pertinent factors (e.g., the reasonable suitability of the reference areas for background comparisons, etc.).

Appendix B. Quality Assurance Project Plan (QAPP)

The QAPP provides the details governing the quality assurance (QA) and quality control (QC) procedures that will be followed in conducting the studies. It also describes the specific protocols concerning sample acquisition, handling and storage, chains-of-custody, and laboratory analysis.

Appendix C. Site Specific Health and Safety Plan (S-HASP)

A site specific health and safety plan (S-HASP) will be developed before implementing work described in the WGS Work Plan. This plan clearly states the relevant health and safety requirements for individuals working during this investigation.

Appendix D. Standard Operating Procedures (SOP)

The Standard Operating Procedures (SOP) provide the procedures that will be followed in the field and laboratory.

Appendix E. Scientific Collector's Permit

Appendix F. Work Scope for the Wild Game Sampling Interim Response Activity

Appendix G. MDEQ limited approval of wild game sampling

2.0 FIELD SAMPLING PLAN

2.1 General Strategy

This sampling plan is designed to simulate as close as possible the harvesting of edible portions of deer, turkey, and rabbits by hunters within the Tittabawassee River floodplain during the Fall hunting season. The primary considerations for this effort are public safety, collection of a representative set of samples, and chain-of-custody and sample integrity issues.

2.2 Sampling Locations

Sampling of wild game animals will generally focus on three portions of the Tittabawassee River (Figure 2-1). One site will be located upstream of Midland along the Tittabawassee River (near Averill, MI), considered to have background environmental concentrations of PCDDs and PCDFs, and will thus serve as a reference site. The second site will be located downstream of the former bridge referred to as Smith's Crossing (i.e., the area on the north side of the river between Smith's Crossing and N. Gleaner Rd.). The third and final site will be located further downstream near Imerman Park.

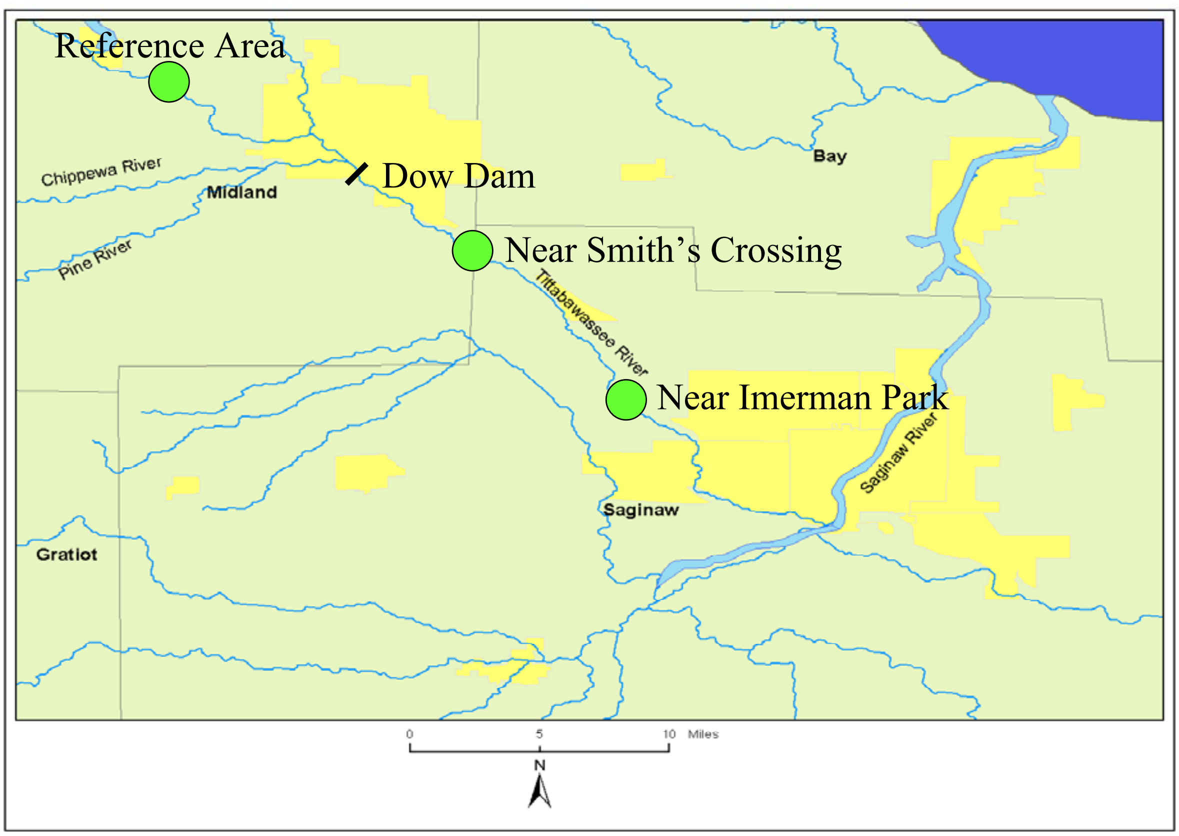

Figure 2-1. Sampling locations for the wild game sampling.

2.2.1 Reference Area

One site will be located upstream of Midland along the Tittabawassee River (near Averill, MI), considered to have background environmental concentrations of PCDDs and PCDFs, and will thus serve as a reference site. Concentrations of PCDDs and PCDFs in the sediments and floodplain soils near the reference area are consistent with statewide background concentrations of TEQs (MDEQ, 2003). The land use can generally be described as primarily mixed agriculture and forest. This area is approximately 9 km upstream of the Dow dam and approximately 15 km upstream of the study area near Smith's Crossing. Thus, taken together with substantial residential, urban, and industrial barriers that are present in this area, this reference area is reasonably far enough removed from the primary study areas to not expect wild game to travel back and forth among these locations. The parcels are all privately owned. Detailed information on the individual parcels is available upon request.

2.2.2 Primary Study Area

There are two additional areas that will be sampled as primary study areas that are located within the floodplain of the Tittabawassee River downstream of Midland. One of these areas is located approximately 6 km downstream of the Dow dam. Specifically, it is located downstream of the former bridge referred to as Smith's Crossing (i.e., the area on the north side of the river between Smith's Crossing and N. Gleaner Rd.). This parcel is owned by The Dow Chemical Company. The land use can generally be described as primarily mixed agriculture and forest.

The final area is located further downstream near Imerman Park (approximately 21 km downstream of the Dow dam). The land use can generally be described as primarily mixed agriculture and forest. Concentrations of TEQs from the floodplain soils in and near Imerman Park were determined for soil samples collected as part of MDEQ's Phase II investigation (MDEQ, 2003). Concentrations of TEQs in these samples ranged up to 2400 ng/kg (on a dry weight basis). Thus, the available data suggest that this area includes elevated concentrations of PCDDs and PCDFs in floodplain soils. The parcels are all privately owned. Detailed information on the individual parcels is available upon request.

2.3 Sampling Objectives

The sampling objectives are dependent on the targeted species. For white-tailed deer, the objective is to harvest a representative sample of male and female deer that are within the age group most targeted by hunters that hunt animals from the Tittabawassee River and its floodplain. Relative to age, every effort will be made to avoid fawns and to try to harvest a similar age structure among locations. However, it may not be possible to match all possible variables. Thus, the influences of variables such as age and gender will be evaluated and discussed as part of the study report. For wild turkey, the objective is also to collect a representative sample of both male and female turkey that would best represent a typical harvest by hunters using these locations since the fall hunt allows hunters to hunt either sex. The decision to collect both sexes for deer and turkey is also based on discussions with MDEQ, USFWS, and MDNR in order to evaluate whether there are gender-specific differences in concentrations of TEQs. For rabbit, the sampling will be more opportunistic rather than targeted in that sex will not be a determinant in the collecting of animals from each location. In the event that rabbits are not abundant (due to habitat suitability-related issues), it may be necessary to substitute squirrels in place of rabbits in the WGS work plan. If squirrels are selected, a single species present in both the reference and the study areas will be targeted for collection. Thus, the methods described below are designed to simulate as close as possible the harvesting of wild game animals by hunters within the Tittabawassee River and its floodplain.

2.4 Target Numbers and Types of Samples to be Collected

Since site-specific historical data are not available for the types of biological samples to be collected, sample size determination was based primarily on logistical constraints to accomplish sampling during the late Fall time period (Table 2-1). Achieving the target numbers of samples will be based on level of effort necessary, the relative abundance of species in the sampling locations, and the success rate of collection methods.

Table 2-1. Target number of samples to be collected at each location.

Organism	Target Number of Samples per Location[1]
White-tailed deer	10-15
Wild turkey	10
Rabbit[2]	10

[1] If the target number of samples cannot be obtained due to limitations on the number of animals that can be collected in a reasonable amount of time, then the scope of this task may be modified.

[2] In the event that rabbits are not abundant (due to habitat suitability-related issues), it may be necessary to substitute squirrels in place of rabbits in the WGS work plan.

2.5 Sample Designation

Sample labeling, preservation and tracking procedures are described in detail in SOP 214 - Documentation, Preservation, Handling, and Tracking of Samples for Analysis, provided in Appendix D. In addition, for deer, there are some sample specific labeling procedures included in SOP 231 - Standard Method for Field Collection and Processing of White-Tailed Deer (*Odocoileus virginianus*) for Chemical Analyses.

2.6 Sampling Frequency and Duration

Sampling will occur in late Fall of 2003. The three locations will be sampled until the targeted sample size for each species is attained. Thus, the entire sampling effort will be dependent on the presence or abundance of the target species at each site, weather conditions, and sampling success.

2.7 Sampling Methodology and Design

This section details the overall sampling methodology, equipment and techniques to be employed in this sampling effort. The sample collection will be conducted under a Scientific Collector's Permit through the Michigan DNR and with the assistance of USDA's Wildlife Services under a cooperative agreement with ENTRIX. The method of take will include standard firearm hunting practices (primarily shotgun and short-range center-fire rifle). In addition, the use of firearms and spotting lights may be employed if necessary for white-tailed deer and wild turkey. All practices will be conducted in such a way to maximize public safety.

For each animal harvested, the following field observations and measurements will be recorded:

- Sample ID
- Species
- Gender
- General site description
- Photographs
- GPS coordinates
- Date and time of harvest
- Collectors initials

After recording observations and measurements, the sample will be processed as described in the standard operating procedures (SOPs).

2.8 Sample Processing

After samples have been collected and tagged in the field and initial documentation has been completed, samples will be initially processed at a secured field facility. In this facility, wild game specimens will be dressed according to standard hunting practices. The following sections briefly discuss the processing procedures. Specific details of processing are included in the associated SOPs.

2.8.1 Deer Processing

For each deer, the liver will be removed as part of the dressing procedure. The exterior of the liver will be rinsed with nanopure water to remove foreign debris, fur, etc. Depending on the size of the liver available, up to 1000 g will be cut into small cubes (approximately 1 cubic inch), weighed, and transferred into a chemically clean, 1 L I-CHEM jar.

After skinning, edible portions of muscle will be cut away from the rump roast area, tenderloin area, and backstrap area. Each of these muscle/meat groups will be cut into small cubes (approximately 1 cubic inch). The target weights are 500 g of rump roast, 250 g of tenderloin, and 250 g of backstrap. For each muscle/meat group, the cubes will be transferred to a weighing boat until the target weight is approached. The last cube to be added will be trimmed until the target weight is achieved as close as possible. The actual weights for each muscle/meat group will be recorded and then transferred into a single chemically clean, 1000-mL I-Chem jar. All of the liver and muscle samples will be stored on ice and transported to the University Research Containment Facility (URCF) at Michigan State University (MSU). At the URCF, samples will be stored at -20^{0}C until they are homogenized. Once homogenized, the samples will be aliquoted into six chemically clean 125 or 250-mL I-CHEM jars. One jar will be shipped to each analytical laboratory, while remaining jars will be archived at the URCF. Splits will be made available to MDEQ and other interested parties upon request.

Deer heads will be used to estimate age and then be preserved (e.g. frozen). In the case that the decision is made that the deer is safe for human consumption, the deer heads will be submitted to MDNR for testing for bovine tuberculosis (BT) and chronic wasting disease (CWD). If the specimens test negative for BT and CWD, the meat will be processed and donated to charitable organizations.

2.8.2 Turkey Processing

Before dressing, turkeys will be weighed to the nearest gram and examined for sex classification. Sex will be determined by examining the breast feathers of the turkeys. (The feathers of the hen are rounded and buff colored while the feathers of the gobbler are squamate and black-tipped.) Sex of the turkeys may also be determined by the relatively greater height of the gobbler and the presence or absence of a beard or spur. Weight and sex of the turkeys will be recorded in the appropriate field laboratory notebook. All turkeys will be dressed according to standard hunting practices, and edible portions of the muscle tissue will be removed from various points on the body. Approximately 700 g of white meat will be removed from the breast, and approximately 300 g of dark meat will be removed from the legs. All muscle samples will be weighed and cut into approximately 1" cubes. For each muscle/meat group, the cubes will be transferred to a weighing boat until the target weight is approached. The last cube to be added will be trimmed until the target weight is achieved as close as possible. The actual weights for each muscle/meat group will be recorded and muscle tissue will be transferred into a single chemically clean, 1000-mL I-Chem jar. Muscle samples in I-CHEM jars will be immediately placed on ice and transported to the URCF at MSU. At the URCF, samples will be stored at -20^0C until they are homogenized. Once homogenized, the samples will be aliquoted into six chemically clean 125 or 250-mL I-CHEM jars. One jar will be shipped to each analytical laboratory, while any remaining jars will be archived at the URCF. Splits will be made available to MDEQ and other interested parties upon request.

The remainder of each turkey carcass will be placed in a plastic bag and stored frozen until the end of the study. If released for human consumption, the meat will be processed and donated to charitable organizations.

2.8.3 Rabbit and/or Squirrel Processing

Before dressing, rabbit and/or squirrel specimens will be weighed to the nearest gram and examined for sex classification. Sex in the squirrels and rabbits will be determined by examining external sex organs and urethral openings. (Males have a rounded, protruding penile sheath with a rounded urethral opening; females have an elongated vulva with a slit opening.) Weight and sex of the rabbits and/or squirrels will be recorded in the appropriate field laboratory notebook. Rabbits and/or squirrels will be dressed according to standard hunting practices, and all edible portions of the muscle tissue will be removed from various points on the body. Muscle samples will be weighed and cut into approximately 1" cubes and then placed in pre-labeled, chemically clean I-CHEM jars (500 or 1000-mL). Rabbit and/or squirrel muscle samples in I-CHEM jars will be immediately placed on ice and transported to the URCF at MSU. At the URCF, samples will be stored at -20^0C until they are homogenized. Once homogenized, the samples will be aliquoted into four chemically clean 250-mL I-CHEM jars. One jar will be shipped to each analytical laboratory, while any remaining jars will be archived at the URCF. Splits will be made available to MDEQ and other interested parties upon request.

The remainder of each rabbit and/or squirrel carcass will be placed in a plastic bag and stored frozen until the end of the study.

2.9 Selection of Analytical Suite

Based on available historical data, the primary chemicals of potential ecological concern (COPECs) are the 17 PCDD and PCDF congeners that have chlorine substitution at the 2,3,7,8-postions. Thus, analysis of all samples will include this suite of 17 PCDD and PCDF congeners. In addition, based on input from USFWS, congener-specific analysis of polychlorinated biphenyls (PCBs) will be conducted on a portion of the deer samples to gain an understanding of the relative contribution of PCBs to the total TEQ concentration. This will be conducted at a rate of one out of every four deer muscle samples. Lipid and moisture content will be determined for all samples.

2.10 Analytical Methodology and Detection Limits

The Limits of Detection (LODs) are based on currently acceptable laboratory performance for certified EPA standard methods 1613 and 8290. The analysis of PCDD/F congeners is particularly susceptible to matrix-based interferences that can significantly alter sample-specific detection limits. Therefore, the data quality objectives provided in Table 2-2 must be considered as 'targets' and not absolute criteria. All efforts shall be made by the laboratory to attain these detection limits. In addition, exceedance of any of these targets for a laboratory (reagent) blank sample would require reanalysis of that batch of samples. Standard reference materials will be included in the samples analyzed. However, standard reference materials do not exist for these specific tissue types, the most suitable available substitutes will be used. In addition, matrix spike samples based on the collected tissues will also be analyzed.

Table 2-2. Target Detection Limits.

Chemical	LOD (pg/g)
2378-TCDD	0.1
2378-TCDF	0.1
12378-PeCDD	0.3
12378-PeCDF	0.3
23478-PeCDF	0.3
123478-HxCDD	0.5
123678-HxCDD	0.5
123789-HxCDD	0.5
123478-HxCDF	0.5
123678-HxCDF	0.5
234678-HxCDF	0.5
123789-HxCDF	0.5
1234678-HpCDD	0.5
1234678-HpCDF	0.5
1234789-HpCDF	0.5
OCDD	1
OCDF	1
TOTAL WHO-TEQ	**0.9**

Chemical	LOD (pg/g)
PCB#77	0.05
PCB#81	0.05
PCB#126	0.005
PCB#169	0.02
PCB#105	0.05
PCB#114	0.05
PCB#118	0.05
PCB#123	0.05
PCB#156	0.05
PCB#157	0.05
PCB#167	0.5
PCB#189	0.05
TOTAL WHO-TEQ	**0.8**

2.11 Study Area Facilities

After samples have been collected and tagged in the field and initial documentation has been completed, samples will be initially processed at a secured field facility. In this facility, wild game specimens will be dressed according to standard hunting practices, tissue samples will be collected and prepared for shipment to Michigan State University's Aquatic Toxicology Laboratory for further processing of samples (i.e., homogenization and separation of sample into aliquots). During wild game specimen processing, all facility surfaces and equipment will be made chemically clean by acetone/hexane rinse. The field and laboratory facilities are equipped with refrigerated and freezer storage, and will be locked in order to secure samples.

2.12 Health and Safety

Health and safety requirements which are applicable to persons who perform work on the Site and or reference area pursuant to this WGS Work Plan are described in the S-HASP. In addition to the normal considerations of health and safety for the personnel conducting the work, the WGS Work Plan is also designed to keep public safety a primary consideration as well since firearms are involved. In addition, notifications will be made to appropriate law enforcement officers, 911 dispatchers, and Michigan DNR Conservation Officers at times when the sampling is scheduled to occur. The S-HASP describes known hazardous substances at the Site, exposure limits, and contingency plans for the WGS Work Plan field work.

2.13 Reporting of Analytical Results

2.13.1 Descriptive Statistics

Descriptive statistics of the results will be reported for all samples collected from the reference and downstream locations. For each sample, results will include percent moisture, percent lipids, congener-specific concentrations of PCDDs, PCDFs, and PCBs, when analyzed, on a wet weight and lipid-normalized basis, and concentrations of total TEQs. In addition, TEQs for each congener and percent contribution of each congener to the total within a sample will be compiled. Descriptive statistics will include the range, arithmetic mean, 95 percent confidence limits on the arithmetic mean, median, geometric mean, standard deviation, and standard error. One-half of the detection limit (DL) will be substituted for any non-detect concentrations. In addition, descriptive statistics will be provided for concentrations of individual PCDD, PCDF, and PCB congeners, when analyzed, and total TEQs (on a wet weight and lipid normalized basis) by site, species, and tissue.

2.13.2 Comparative Statistics

Comparative statistics for each species between different locations will be conducted with concentrations of TEQs on a wet weight basis. In addition, a comparison will be made for congener patterns. The specific strategies for conducting the statistical analyses and for making decisions are outlined below and are detailed in the Decision Procedure Document.

Statistical comparisons of the data will be conducted to provide answers to specific questions related to differences in PCDD/PCDF congeners in samples collected from the upstream reference area and downstream locations. As a result, these questions can be formulated as null and alternative hypotheses where the criteria for acceptance or rejection of these testable hypothesis specifies a significance of a Type I or Type II error. For these analyses, a significance of probability for Type I error (α) should be less than (<) 0.05 while the probability for Type II error (β) should be less than (<) 0.2 [producing power as $(1-\beta) > 80\%$]. The specifics of these parameters are given in greater detail in the Decision Procedure Document.

The initial step in the evaluation of data from the wild game samples collected at the upstream reference and downstream locations, will be to determine if the data meet the requirements for use of parametric statistical tests such as normality of the data distribution and homogeneity of variance. If the data do not meet the normality requirement, all data will be log transformed and the normality and variance homogeneity tests will be reapplied. If either the non-transformed or log-transformed data meet both parametric requirements, TEQ concentrations at the various locations will be compared using standard parametric statistical tests such as a protected (F-test) analysis of variance (ANOVA) for a comparison across all sites or a Student's t-test when only two sites are being compared. If significant differences in TEQ concentrations are determined in the ANOVA test, then a subsequent analysis of the data using a means comparison test (such as a Dunnett's test) will be conducted to examine individual differences between the upstream reference location to the down stream locations. If the data do not meet the requirements for parametric statistical tests, their non-parametric equivalents such as the Kruskal-Wallis or Wilcoxon tests will be used. If no significant differences are observed between locations, a power analysis will be conducted to determine the probability that a Type II error has occurred, that is, that we have accepted a null hypothesis when in fact there are differences between sample locations. If statistically significant differences are observed between the reference location and the downstream sample locations, multivariate profile analysis will be conducted on the data to evaluate the potential sources of these differences between locations. The multivariate statistics will include principle component analysis (PCA) and profile analysis (PA) to evaluate the differences in PCDD and PCDF congener patterns (wet weight) between locations to investigate the potential basis for the differences observed between the locations. Finally, if sufficient data are available for each species, statistical analyses will be conducted to evaluate sex-related differences in TEQ concentrations at each location. Statistical methods used will depend on whether the data meets the criteria for parametric statistics. If the data do meet these criteria, a T-test will be used to evaluate potential differences at each site relative to sex.

3.0 SCHEDULE AND REPORTING

3.1 Schedule

Wild game samples will be collected in late Fall of 2003. Analytical data results are expected to be available by February 2004 and a final report is expected in Spring 2004. The full anticipated schedule including all major elements, sequencing, and estimated timelines for this study is described in the "Work Scope for the Interim Response Activity of Evaluating Wild Game Taken from the Tittabawassee River Floodplain" submitted by Dow and approved by MDEQ on October 21, 2003 (Carrington, 2003; MDEQ, 2003b).

3.2 Reporting

Reports from this project will include all data obtained from the field and laboratory phases of the study. MDEQ will be provided with an electronic copy of the laboratory data packages and field data. If any major deviation from the approved Work Plan are necessary because of unanticipated field conditions, the MDEQ (and MDNR and USFWS, if appropriate) will be notified as soon as possible for approval and modification of the Work Plan, if needed.The chemical and physical data will be statistically analyzed and summarized. The results from study will be used to determine if wild game taken from the Tittabawassee River floodplain downstream of Midland represent a relevant human exposure pathway to PCDDs and PCDFs or not.

The results of these studies will also be published in the scientific literature in order to provide useful data for health professionals, risk assessors and individuals interested in this information.

4.0 REFERENCES

Carrington, S. 2003. Work Scope for the Interim Response Activity of Evaluating Wild Game Taken from the Tittabawassee River Floodplain. Submitted to MDEQ from The Dow Chemical Company, October 20, 2003.

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DRAFT

Appendix A. Decision Procedure Document

DECISION PROCEDURE

FOR THE

DRAFT WORK PLAN FOR THE INTERIM RESPONSE ACTIVITY OF EVALUATING WILD GAME TAKEN FROM THE TITTABAWASSEE RIVER FLOODPLAIN

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East Lansing, Michigan

Prepared for:

The Dow Chemical Company
Midland, Michigan

November 21, 2003

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Definitions and Acronyms

AhR	Aryl hydrocarbon Receptor
ND	Non-detect
LOQ	Limit of Quantitation
PCDD	Polychlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzofuran
TCDD	2,3,7,8-Tetrachlorodibenzo-p-dioxin
TEQ	TCDD equivalents
TEF	Toxicity Equivalency Factors
WGS	Wild Game Sampling
WHO	World Health Organization

1.0 INTRODUCTION

This decision procedure is an attachment to the draft Wild Game Sampling (WGS) Work Plan for the Tittabawassee River Floodplain near Midland, Michigan. The decision procedure will be used to evaluate tissue residue data on polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in samples of wild game, including tissues from white-tailed deer, wild turkeys, and rabbits.

Concentrations of the seventeen PCDD and PCDF congeners substituted with chlorines at positions 2, 3, 7, and 8, are routinely converted to TCDD equivalents (TEQs) using the 1998 World Health Organization (WHO) toxic equivalency factors (TEFs; Van den Berg et al., 1998). In this document, instrumental chemical residue analyses of PCDD and PCDF congeners denote strict determinations of chemical concentration on a wet weight basis. Furthermore, throughout this document the term "TEQ" will be used to describe 2,3,7,8-TCDD equivalents that are calculated by summing the analytical concentrations of PCDD/F congeners adjusted by their TEF values. Thus, the decision procedure will be based on the toxic equivalency (TEQ) approach. The rationale for this approach is discussed later in this document and specific details of these calculations are presented in Section 1.4 of the draft WGS Work Plan.

This Decision Procedure is designed to answer the general question:

Are concentrations of TEQs in wild game collected from the Tittabawassee River floodplain downstream of Midland significantly greater than concentrations of TEQs in samples of the same tissues from the same species collected at an upstream reference location?

This Decision Procedure provides an objective, statistically based approach in order to determine if concentrations of TEQs are elevated in wild game animals collected from the Tittabawassee floodplain downstream of Midland. The sampled wild game animals will likely integrate potential exposures to PCDDs and PCDFs over relatively large areas on the Tittabawassee floodplain and will be collected at times that correspond with hunting activities. Thus, these samples should cover the area of interest spatially and temporally and be representative of the relevant exposure pathways. The main purpose of this document is to specify decision procedures for: 1) statistical analyses of concentrations of TEQs and congener patterns, and 2) the overall conclusions for various results from the testing of specific hypotheses. These procedures and conclusions are designed to yield unequivocal answers to specific questions posed as hypotheses directed at wild game tissue samples. Statistical tests of these hypotheses will enable ENTRIX, Inc. and other interested parties, to make scientifically defensible conclusions about the probability of greater concentrations of TEQs in wild game samples from the Tittabawassee River floodplain downstream of Midland. Risk-based recommendations on the outcome of these results will be provided.

The following sections provide the background and rationale for the decision procedure. In particular, Section 2.0 provides a description of aggregate measures of concentrations and toxicity equivalence factors. Section 3.0 discusses the statistical methods that will be used in the analyses. Section 4.0 states the main questions in this study as null and alternative hypotheses, and Section 5.0 contains the detailed decision procedure in an outline format. Section 6.0 contains flowcharts for the decision procedures. References are provided in Section 7.0.

2.0 BACKGROUND

As described in the WGS Work Plan, muscle tissue from wild game animals (white-tailed deer, wild turkey, and cottontail rabbits) and liver tissue from deer will be homogenized, extracted, and analyzed for concentrations of the seventeen 2,3,7,8-substituted PCDD and PCDF congeners by HRGC/HRMS. Results of the tissue residue analyses will be used as an operational measure of the total concentrations of TEQs and will determine if wild game from locations downstream of Midland contain significantly greater concentrations of TEQs than those collected from an upstream reference location.

This decision procedure specifies how concentrations of TEQs in wild game collected from locations downstream of Midland will be statistically compared to concentrations in wild game collected at a reference location upstream of Midland. If concentrations of TEQs in samples collected downstream of Midland are significantly ($p < 0.05$) greater than those at an upstream reference site, this result will provide support for the inference that wild game downstream of Midland are exposed to TEQs from floodplain soils downstream of Midland. If concentrations of TEQs in wild game downstream of Midland are not significantly greater than those upstream of Midland, this outcome will provide support for the inference that wild game downstream of Midland are not exposed to TEQs above reference concentrations. Furthermore, this study will provide information on the general biological availability of PCDDs and PCDFs in wild game tissues, and this information can be used to determine if wild game taken from the Tittabawassee River floodplain represents a relevant human exposure pathway to PCDDs and PCDFs.

The strength of these inferences, however, will depend on the statistical power of the study to actually detect differences that truly do exist, on the quality of data generated by instrumental analyses, and on the representativeness of the samples that are collected.

2.1 Use of TEQs

PCDDs and PCDFs are mixtures of as many as 210 individual chemical congeners, 75 PCDDs and 135 PCDFs. The relative concentrations of these individual congeners vary among samples. In addition, the relative toxic potency of the individual congeners varies over several orders of magnitude. Thus, it is not possible to determine the toxic potency of these mixtures solely by determining the total PCDD and PCDF concentrations as a sum of congener concentrations. To determine whether potential toxic effects of concentrations of PCDD and PCDF are significantly greater in wild game samples from locations downstream of Midland as compared to concentrations from an upstream reference area, it is necessary to combine concentrations of PCDD and PCDFs into a single aggregated measure of TEQs. In this way, there will be a common metric (i.e., concentrations of TEQs) for comparative statistical evaluation of wild game samples from upstream and downstream locations and for evaluation of potential human risk. While the focus of this investigation is not polychlorinated biphenyls (PCBs), it should be noted that 4 non-*ortho*- (co-planar) and 8 mono-*ortho*-substituted PCBs also exhibit AhR activity. In order to conduct a preliminary assessment of the relative contribution of PCB congeners to total TEQs, the WGS Work Plan includes limited sampling for PCBs in about 25% of the deer muscle tissues. However, since concentrations of PCDDs and PCDFs are the focus in this study, only PCDDs and PCDFs will be used to calculate concentrations of TEQs in wild game animals.

Concentrations of TEQs are typically expressed in units of picogram TEQs per gram of sample (pg TEQs/g sample, or ppt). It is proposed that this assessment will be conducted based on wet weight normalization since this is most commonly used normalization method for presenting concentrations in food items and is also the conventional approach for deriving estimates of potential dietary exposure. However, information on lipid content will be provided so that lipid-normalization can also be conducted. In this decision procedure, the values used for TEF were developed by the WHO, and are based on an expert review of available toxicity information for all PCDD and PCDF congeners (Van den Berg et al., 1998). The advantage of this TEQ method is the ability to potentially identify and quantify each of the seventeen AhR active PCDD and PCDF congeners in samples, whereby results can be used to examine patterns of contamination and relative contributions of congeners to TEQs. Disadvantages include quantitative uncertainties due to non-detectable congeners, chemical interferences, and problems with uncertainties in TEFs.

2.2 TEQs and Congener Patterns

TEQs provide useful and relevant aggregate measures of the overall potency of the mixture of PCDDs and PCDFs. In addition, the statistical comparisons of TEQs in wild game animals will be integral in making decisions regarding the estimation of risk toward human health. However, TEQs do not utilize all of the information provided by the suite of measurements of congener concentrations. Accordingly, if TEQ concentrations differ between upstream and downstream locations, an additional method of statistical analysis will be used to investigate patterns of relative congener concentrations between the various sampling locations. Analyses of congener patterns will help identify which congeners are present at elevated concentrations in wild game animals downstream, and may suggest the spatial pattern of contamination within the area, but will not be useful when estimating risk toward human health. Therefore, TEQs and congener patterns will be used to investigate concentrations of PCDD/Fs from upstream and downstream of Midland, however only TEQ analyses will be used in estimations of risk.

3.0 STATISTICAL METHODS

3.1 Tests For Normality And Homogeneous Variances

Before hypothesis tests are conducted, data sets will be evaluated to determine if parametric or non-parametric statistics will be used in the analyses. Parametric statistics assume that the data distribution is normal or bell-shaped and the variances of each population are homogeneous (equal). Non-parametric statistical tests are not dependent on a specific distribution; rather, they are "distribution-free" and can be used to test the distribution of data relative to different types of distribution functions. The data from each site will first be tested for a normal distribution by using the One Sample Kolmogorov-Smirnov test with Lillifor's transformation (Wilkinson, 2000). If data for a species and or tissue type at a location are not normally distributed, then the data will be log-transformed and the data set re-tested. To determine if the variances are homogeneous in the data sets, one of two tests will be used depending on the number of locations being evaluated. For two locations, the variances of samples collected from each of the reference and downstream locations will be tested by an F-Test. If greater than 2 locations are to be evaluated, a Levene's Test will be conducted to evaluate variance homogeneity (Wilkinson, 2000). If the data are not normally distributed or do not have homogeneous variances, then the use of parametric statistics becomes suspect and the results difficult to interpret. Under this scenario a non-parametric statistical test would be used for comparisons of TEQ concentrations among locations.

3.2 Statistical Comparisons Of TEQs

In all cases statistical analyses will be conducted with concentrations of TEQs derived from the concentrations and relative potencies of the 7 PCDDs and 10 PCDFs that exhibit AhR agonist activity. Separate analyses will be performed for each species to test for differences in concentrations of total TEQs among sample locations.

The general approach to evaluate differences in TEQ concentrations for wild turkey, rabbit and/or squirrel samples is as follows. If data from wild game samples meet the requirements for parametric tests, then a Student's t-test (equal sample sizes) or the tabled t-test (unequal sample sizes) will be used to compare TEQs between two locations. If three locations are compared, an ANOVA with Tukey's Honestly Significant Difference (HSD) will be used to compare TEQs among locations (Wilkinson, 2000). If data are not normally distributed and do not meet the criteria for homogeneous variances, then non-parametric statistical tests will be used to evaluate differences between or among locations. If only two locations are to be tested, a Mann-Whitney U test will be used to evaluate differences between locations. If greater than 2 locations are to be evaluated, then the Kruskal Wallis test will be used for statistical analyses (Wilkinson, 2000). In all cases, one-tailed statistical tests will be used to evaluate potential differences between the upstream reference location and the downstream locations. One-tailed statistical tests tend to have a greater ability to detect smaller differences between populations, reducing the probability of a Type II error.

The general approach to evaluate differences in TEQ concentrations for white-tailed deer samples is as follows. If white-tailed deer data meet the requirements for parametric tests, a two-factor ANOVA will be used to concurrently evaluate the effects of location and sex on total TEQ concentrations (Wilkinson, 2000). If sex is not a significant factor, then both male and female deer samples will be combined, and a one-factor ANOVA will be conducted. If significantly different, then a Tukey's HSD test will be used to evaluate differences between locations. If data are not normally distributed and do not meet the criteria for homogeneous variances, then non-parametric statistical tests will be used to evaluate differences between or among locations. If only two locations are to be tested, a Mann-Whitney U test will be used to evaluate differences between locations. If greater than 2 locations are to be evaluated, then the Kruskal Wallis test will be used for statistical analyses (Wilkinson, 2000). In all cases, one-tailed statistical tests will be used to evaluate potential differences between the upstream reference location and the downstream locations. One-tailed statistical tests tend to have a greater ability to detect smaller differences between populations, reducing the probability of a Type II error.

As an integral step in the statistical evaluation, the appropriate treatment of non-detect (ND) data will be evaluated. This will be accomplished by conducting a sensitivity analysis to determine the effect of varying values for ND data. Specifically, this will be accomplished by calculating TEQ concentrations based on substituting various proxy values for congeners that are less than their limit of quantitation (LOQ). The proxy values that will be used to calculate TEQ concentrations will be the following: ND=0, ND=1/2 LOQ, and ND=LOQ. However, if the proportion of non-detect values is greater than 50%, and sample size permits, it might be possible to develop more sophisticated estimates of values for ND congeners (Helsel, 1990). This approach would involve the use of distributional methods (regression on order statistics, ROS) such as maximum likelihood estimates (MLE). In this method, observed data are used to estimate summary statistics of the distribution assumed to represent the underlying chemical concentrations at the location. Another approach would be the use of a distributional method to estimate data values corresponding to the percentiles of non-detect values. These estimates replace the non-detected values in the data set, and summary statistics are calculated from the data set containing both the reported and surrogate values.

3.3 Statistical Criteria

The criteria for acceptance or rejection of all testable hypotheses specifies a significance of probability for committing a Type I error (false positive claim) and the probability for Type II error (false negative claim). Thus, in this study the significance level for a Type I error (α) will be less than (<) 0.05 [providing confidence as (1- α) greater than (>) 95%] and a probability for Type II error (β) to be less than (<) 0.20 [producing power as (1-β) > 80%] (Salsburg, 1986). The Type II error rate (β) depends on four main factors; specified α, available sample size, sample variance, and the selected relative effects distance (Equation 1).

$$n = \frac{\left(z_\alpha + z_\beta\right)^2 * \sigma^2}{\delta^2} \qquad \text{(Equation 1)}$$

Where n is the sample size, z_α and z_β are the standard normal deviates associated with α and β, respectively, σ^2 is the population variance for TEQ concentrations, and δ is the relative effects distance (difference) chosen for the analysis. Shown in Equation 1, the magnitude of the relative effects distance is linked to sample size, variance of the populations and the probabilities of a Type I (α) and Type II (β) error used in the statistical analysis.

When appropriate, a power analysis will be conducted for each test to evaluate the potential for a Type II error (i.e., concluding that there is no difference between locations when in fact there is). For the statistical power tests, the Type I error (α) will be set to 0.05 and the relative effect's distance (difference between locations) will be selected as 3-fold the TEQ concentration found in comparable upstream reference samples. Sample size will be dependent on the number of each species collected at each sampling location. If the results of the power analysis indicate that there is insufficient power (i.e., 1-β less than 0.8), then a sufficient sample size will be estimated to detect differences between locations based on the criteria outlined above.

Unless noted otherwise, the above statistical criteria will be applied in evaluating potential differences between locations for each sample type. However, strict adherence to these requirements should not preclude sound professional observations about the data, such as trends or tendencies with slightly lower levels of statistical significance of α such as $p < 0.1$ or β-values greater than 0.2

3.4 Congener Patterns

If there are statistical differences in total TEQs among upstream and downstream locations, then analyses of the patterns of relative concentrations (frequency and magnitude) of congeners will be evaluated. Congener pattern analyses will be conducted with multivariate statistics, such as Principal Components Analysis (PCA) or other appropriate discriminate analyses, including cluster analyses and/or canonical correlations. PCA identifies linear combinations of standardized congener concentrations that best explain the overall variance in the data. These linear combinations are known as Principal Components (PCs). The PCs are calculated and can be plotted in a multidimensional array to allow visualization of locations of data that are most similar. While PCA provides a mechanism for combining data in such a way that the maximum discrimination power is concentrated on a reduced number of variables, it does not provide a rigorous test of which samples are statistically dissimilar. A null hypothesis relative to individual locations can not be tested using PCA, because PCA is basically a data reduction technique used to reduce the number of variables from a larger set describing the multivariate state and space of a group of samples. Once PCs are established for standardized concentrations, then a profile analysis will be conducted. Profile Analysis (Morrison 1976) will be used to test for differences in the relative concentrations of congener distributions. This test consists of a multivariate analysis of variance (MANOVA) of the differences in the concentrations of individual congeners, followed by a Hotelling's t-test to test for statistical differences among sample populations. A non-parametric test can be performed if results are not normally distributed, or boot-strapping may be considered for use.

4.0 NULL AND ALTERNATIVE HYPOTHESES

The statistical comparisons of the data that are outlined above will provide answers to the following questions, which are formulated as null and alternative hypotheses.

4.1 Hypotheses Stated to Compare TEQs

$H1_0$: *Mean concentrations of TEQs are **not greater** in samples from locations downstream of Midland, including Smiths Crossing (S) and Imerman Park (I), when compared to samples from an upstream reference (R) population.* [H_o: $\mu_S = \mu_I = \mu_R$]

$H1_a$: *Mean concentrations of TEQ, are **greater** in samples from one or both locations downstream of Midland, including Smiths Crossing (S) and/or Imerman Park (I), when compared to samples from an upstream reference (R) population.* [H_a: $\mu_S > \mu_R$ or $\mu_I > \mu_R$ or μ_S, $\mu_I > \mu_R$]

Note: The null hypotheses will be tested separately for white-tailed deer muscle samples, white-tailed deer liver samples, wild turkey muscle samples, and rabbit muscle samples.

4.2 Hypothesis Stated to Compare Congener Patterns

$H2_0$: *Patterns of relative concentrations (ratios of congeners) of PCDD/Fs are not different in samples from locations downstream of Midland (D) compared to patterns in samples in the same species from an upstream reference (R) population.* [H_o: $\mu_D = \mu_R$]

$H2_a$: *Patterns of relative concentrations (ratios of congeners) of PCDD/Fs are **different** in samples from locations downstream of Midland (D) compared to patterns in samples in the same species from an upstream reference (R) population.* [H_o: $\mu_D \neq \mu_R$]

Note: The null hypothesis will be tested separately for white-tailed deer muscle samples, white-tailed deer liver samples, wild turkey muscle samples, and rabbit muscle samples.

5.0 DECISION PROCEDURE OUTLINE

This section outlines five steps. Procedures for compiling and assessing the acceptability of the data are found in Section 5.1. Procedures for conducting statistical analyses on TEQs are found in Section 5.2, and the decision criteria to be applied to the results of these statistical tests to answer the principle question for this study is found in Section 5.3. Procedures for evaluating risk toward human health are found in Section 5.4. Congener analyses are specified in section 5.5.

5.1 Data Acceptability (STEP I)

Data will be validated and assessed for acceptability. Quality assurance and quality control (QA/QC) will be conducted per the procedures specified in the Work Plan. Data will be compared to the data quality objectives (DQOs) developed in the sampling and analysis plan.

1. If all DQOs that are specified in the Work Plan are met, the data will be classified as "fully acceptable", then proceed to Step II below.
2. If data do not meet all the DOQ values for acceptability, but do meet some of the minimal criteria outlined in the Work Plan, the data will be classified as "usable". However, the results and conclusions will be annotated with the significance of the short-comings and fully described in the uncertainty sections of reports. For example, flagged data will be assessed for relative impact on quantitative results. Proceed to Step II below.
3. If data fail to meet any of the criteria in item 2 above, ENTRIX, Inc. will decide how to proceed in regards to the less-certain usability of the data; e.g., recoveries may be too far from 100%, or interferences may cause the MDL to be too high. These data may be partially useful and sufficient for semi-quantitative analyses, rather than for quantitative statistical analyses, as performed in Steps II and III below.

5.2 Calculations And Statistical Comparisons Of TEQs (STEP II)

5.2.1 Data set calculations for statistical analyses

Total TEQ concentrations will be calculated for white-tailed deer, wild turkeys, and rabbits. For each species and tissue type, TEQ concentrations will be calculated several different ways to evaluate the effects of assigned proxy values in subsequent statistical analyses. TEQs should be calculated in the following manner:

1. Select validated data for all seventeen AhR-active 2,3,7,8-substituted PCDDs or PCDFs.
2. Calculate TEQ concentrations based on the three different sets of data below:
   - (A) ND = 0: In this data set all congeners that are below the LOQ will be assigned proxy values equal to zero.
   - (B) ND = ½ LOQ In this data set all congeners that are below the LOQ will be assigned proxy values equal to ½ the LOQ.
   - (C) ND = LOQ In this data set all congeners that are below the LOQ will be assigned proxy values equal to the LOQ.
3. To compute the 2,3,7,8-TCDD equivalent concentration (TEQ) (pg/g) for each analyte (congener) in each sample, multiply the appropriate WHO TEFs by the congener concentration, and sum these

products over all congeners to produce the sample TEQ as an aggregate measure of toxicity (Equation 2). For congeners with TEFs reported as less than (<) values, use the numerical part of the less than TEF value. Effects of this substitution can also be examined later in the sensitivity analysis, where the less than TEF value will instead be set to zero.

$$TEQ = \sum_{i \to n} [(Congener_i \times TEF_i) + ...(Congener_n \times TEF_n)] \qquad \text{Equation 2}$$

4. To evaluate the sensitivity of the data set to assigned proxy values, all three TEQ data sets (ND=0, ND = ½ LOQ, ND = LOQ) will be evaluated in statistical comparisons.

5.2.2 Statistical comparisons of TEQs

Statistical tests for white tail deer, wild turkey, and rabbit tissues will be conducted as described in detail in this section of the document. Only deer samples will be analyzed for gender differences in total TEQs.

5.2.2.1 Testable Hypotheses for White-tailed Deer, Turkey, and Rabbit Tissues among All Locations:

$H2_0$: *Mean concentrations of TEQs are **not greater** in samples from locations downstream of Midland, including Smiths Crossing (S) and Imerman Park (I), when compared to samples from an upstream reference (R) population.* [H_o: $\mu_S = \mu_I = \mu_R$]

$H2_a$: *Mean concentrations of TEQ, are **greater** in samples from one or both locations downstream of Midland, including Smiths Crossing (S) and/or Imerman Park (I), when compared to samples from an upstream reference (R) population.* [H_a: $\mu_S > \mu_R$ or $\mu_I > \mu_R$ or μ_S, $\mu_I > \mu_R$]

2. Categorize data into three groups: upstream reference (R), downstream Smiths Crossing (S) and downstream Imerman Park (I).

3. For the data sets described above, determine if data are normally distributed and have homogeneous variance. Test for statistically significant ($p < 0.05$ for α) increases in concentrations of TEQ in (S, I) > (R) and for (S)>(I); evaluate tests for power ($p < 0.20$ for β) to detect a group mean difference of at least 3-fold:

   (A) If TEQs are normally distributed in each group, then use one-way protected ANOVA followed by Tukey's HSD multiple comparison test to test if: (S)>(R), (I)>(R), or (S)>(I);

   or

   (B) If TEQ values are not normally distributed but are log normal, use a one-way protected ANOVA followed by Tukey's HSD multiple comparison test on log-transforms to compare if: (S)>(R), (I)>(R), or (S)>(I);

   or

   (C) If TEQ values are neither normal nor log-normal, then use the Kruskall-Wallis test followed by the Mann-Whitney U test to compare if (S)>(R), (I)>(R), or (S)>(I).

5.3 Overall Decision Analysis Of Statistical Data (STEP III)

A flowchart for the overall decision analysis is presented in Section 6.0 below (Figure 6-3). The following question originally posed in Section 1.0 of this document, will be answered by a weight (amount) and strength (quality) of evidence approach:

Are concentrations of TEQs in representative wild game samples collected from locations downstream of Midland significantly greater than concentrations in comparable samples from upstream of Midland?

It should be noted that the following section requires perspective on the scientific caveats related to the design and results of this study. Briefly, these main caveats are summarized below.

- Concentration in this context means toxic-equivalents of 2,3,7,8-TCDD generated by the seventeen PCDD and PCDF congeners that have AhR agonist activity.
- An inconclusive decision indicates that the general question posed can not be answered "yes" or "no" with confidence. An inconclusive outcome will result in further analysis by ENTRIX, Inc. to determine potential causes and solutions to this outcome.

5.3.1 Decision procedure for TEQs in white-tailed deer, turkeys, and rabbits

Compare the outcomes of the statistical analyses for TEQ concentrations in Step II for white-tailed deer liver and muscle samples, and repeat this process for wild turkey and rabbit muscle sample data.

1. If concentrations of TEQs are significantly different ($p < 0.05$) between upstream and downstream locations, then evaluate the impact of proxy values on the data set.

(A) If proxy values constitute <u>"less than half" the concentration of TEQ for 50 percent or more</u> of the samples, then there is low impact of proxy values on the data set. Conclude:

Mean concentrations of TEQs are greater in samples from downstream of Midland (S and I) when compared to samples at an upstream reference location (R). Proceed to Step IV and conduct congener pattern analysis.

(B) If proxy values constitute <u>"more than half" the calculated TEQ for 50 percent or more</u> of the samples, then there is high impact of proxy values on the data set. Examine TEQ concentrations.

1. If the concentrations of TEQs for all samples are less than 3-fold of the TEQ concentration based on LOQs for targeted congeners, then conclude:

Mean concentrations of TEQs are not greater in samples from downstream of Midland (S and I) when compared to samples at an upstream reference location (R). Proceed to Step IV.

2. If the TEQ concentration for any sample is greater than 3-fold the TEQ concentration based on LOQs for targeted congeners, then conclude:

The outcome is inconclusive. Proceed to Step IV.

2. If concentrations of TEQs are not significantly different ($p > 0.05$) between upstream and downstream locations, then evaluate the statistical power ($1-\beta$) associated with the analysis.

    (A) If statistical power ($1-\beta$) is greater than 80% for comparisons (based on a minimum detectable difference of 3-fold the reference TEQ concentration), then accept the null hypotheses and conclude:

Mean concentrations of TEQs are not greater in samples from downstream of Midland (S and I) when compared to samples at an upstream reference location (R). Proceed to Step IV.

    (B) If statistical power ($1-\beta$) is less than 80% for the comparisons (based on a minimum detectable difference of 3-fold the reference TEQ concentration), then the null hypotheses can not be accepted because of a lack of statistical power and:

The outcome is inconclusive. Proceed to Step IV.

5.4 Evaluation of Potential Human Health Risk (STEP IV)

In this step, the final decisions concerning potential human exposure and risk to groups that consume wild game from the Tittabawassee River floodplain are addressed. The basic decision to be made can be stated as follows:

> *Do concentrations of TEQs in wild game pose an unacceptable risk to people that hunt and consume wild game within the Tittabawassee River floodplain downstream of Midland?*

Factors to be considered in this evaluation include, yet are not limited to, the potential incremental risk relative to the reference samples, comparison to concentrations of TEQs from other sources of protein that have been measured as part of recent market basket surveys, exposure factor assumptions relative to wild game consumption, and uncertainties. Probabilistic risk assessment, incorporating probability distribution function data on key exposure parameters, will be used to assess theoretical increases in incremental risk due to consumption of wild game.

5.5 Statistical Comparison of Congener Patterns

If there are statistical differences in TEQ concentrations between upstream and downstream locations, statistical comparisons of congener patterns will be conducted. Statistical comparisons of congener patterns will be conducted to determine whether significant differences exist between congener patterns in target species upstream and downstream of Midland, which might indicate a possible source for these targeted compounds. The first phase of the analysis will be a principal component analysis (PCA), which is favored as an initial step in this analysis. This statistical procedure retains all the variability inherent in the data set while allowing for simple graphical presentation of the data. This analysis provides great sensitivity for detecting semi-quantitative differences between groups. Should PCA indicate differences between sample groups, then a detailed Profile Analysis (Morrison 1976) will be conducted. The main advantage of this analysis over PCA is that it uses the unmodified sample data rather than contriving a series of orthogonal synthetic variables such as done in PCA. Statistical analysis can therefore be conducted on the raw data focused upon the subset of congeners in the PCs, as opposed to the synthetic PCA variables, ensuring greater statistical rigor.

5.5.1 Data set calculations for statistical analyses

1. Select data for only the seventeen active 2,3,7,8-substituted PCDDs and PCDFs so as to evaluate the ratios of PCDD and PCDF congeners.
2. Calculate congener concentrations based on the three different proxy value assignments for ND samples.
   - (A) ND = 0: In this data set all congeners that are below the LOQ will be assigned proxy values equal to zero.
   - (B) ND = ½ LOQ In this data set all congeners that are below the LOQ will be assigned proxy values equal to ½ the LOQ.
   - (C) ND = LOQ In this data set all congeners that are below the LOQ will be assigned proxy values equal to the LOQ.
3. To evaluate the sensitivity of the data set toward proxy values, all three data sets (ND = 0, ND = ½ LOQ, ND = LOQ) will be evaluated in pattern analyses.

5.5.2 Pattern analysis

Pattern analyses tests for white tail deer, wild turkey, and rabbit tissues will be conducted as described in detail in this section of the document.

5.5.2.1 Testable Hypothesis: Congener Patterns

$H4_o$: *Patterns (ratios) of relative concentrations of PCDD and PCDF congeners are the* ***same*** *in samples from downstream (S and I) of the Midland compared to patterns in samples in the same species from an upstream reference (R) population.* [H_o: $\mu_s = \mu_R$, $\mu_I = \mu_R$]

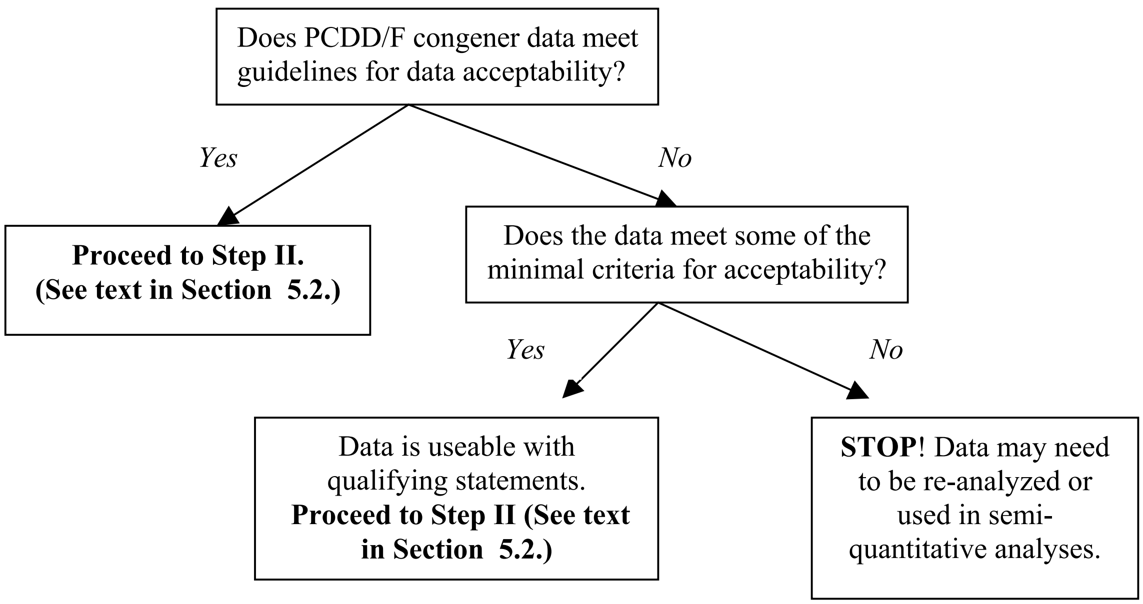
$H4_a$: *Patterns (ratios) of relative concentrations of PCDD and PCDF congeners are* ***different*** *in samples from downstream (S and I) of the Midland compared to patterns in samples in the same species from an upstream reference (U) population.* [H_o: $\mu_s \neq \mu_R$, $\mu_I \neq \mu_R$]

1. Group data spatially, as below and then run pattern analysis.
   - (A) For white tail deer muscle and liver samples, categorize the samples as (S), (I) and (R).
   - (B) For wild turkey and rabbit muscle samples, categorize muscle samples as (S), (I) and (R).
2. Run PCA on the data set using standardized congener concentrations. Each congener at a location is standardized as: ([value - mean]/ standard deviation). Select the most important (~2-4) principal components. If needed, correlation analysis or cluster analysis can be used to select the subset of congeners for subsequent use in profile analysis.
   - (A) Prepare scatter plots and examine visually for separation between groups.
   - (B) If separations are apparent, conduct Profile Analysis with Hotelling's t-test, or other appropriate non-parametric test, as above.

6.0 TABLES AND FIGURES

STEP I

art for data acceptability of TEQs in white tailed deer, wild turkey, and



STEP II

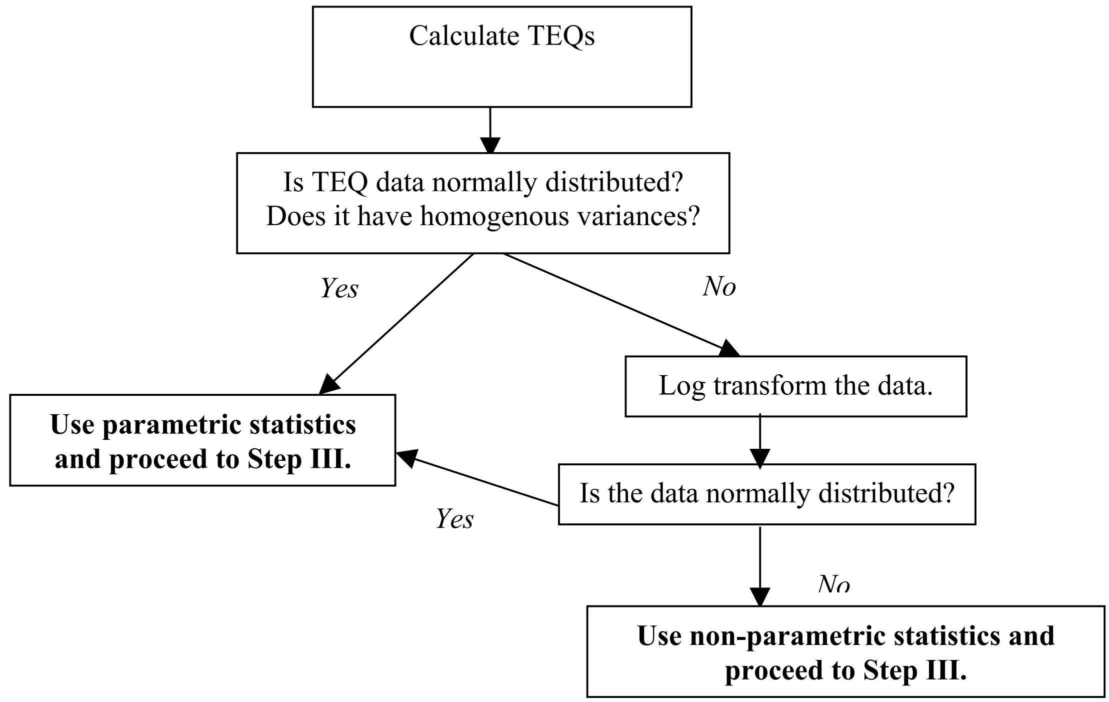


Figure 6-2. Flowchart for TEQ concentrations in white-tailed deer, wild turkey, and rabbits, STEP II.

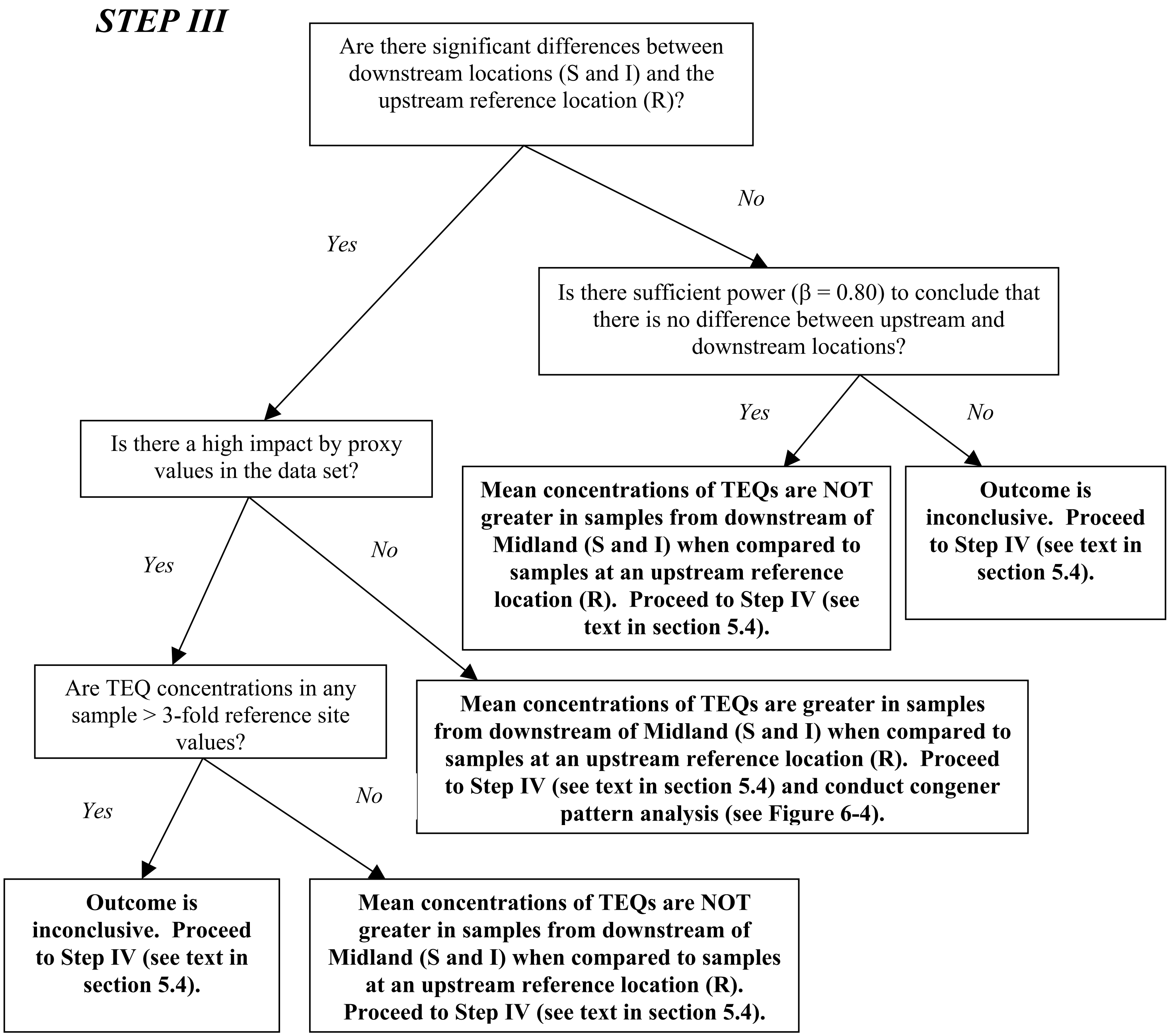


Figure 6-3. Overall decision procedure for statistical results, STEP III

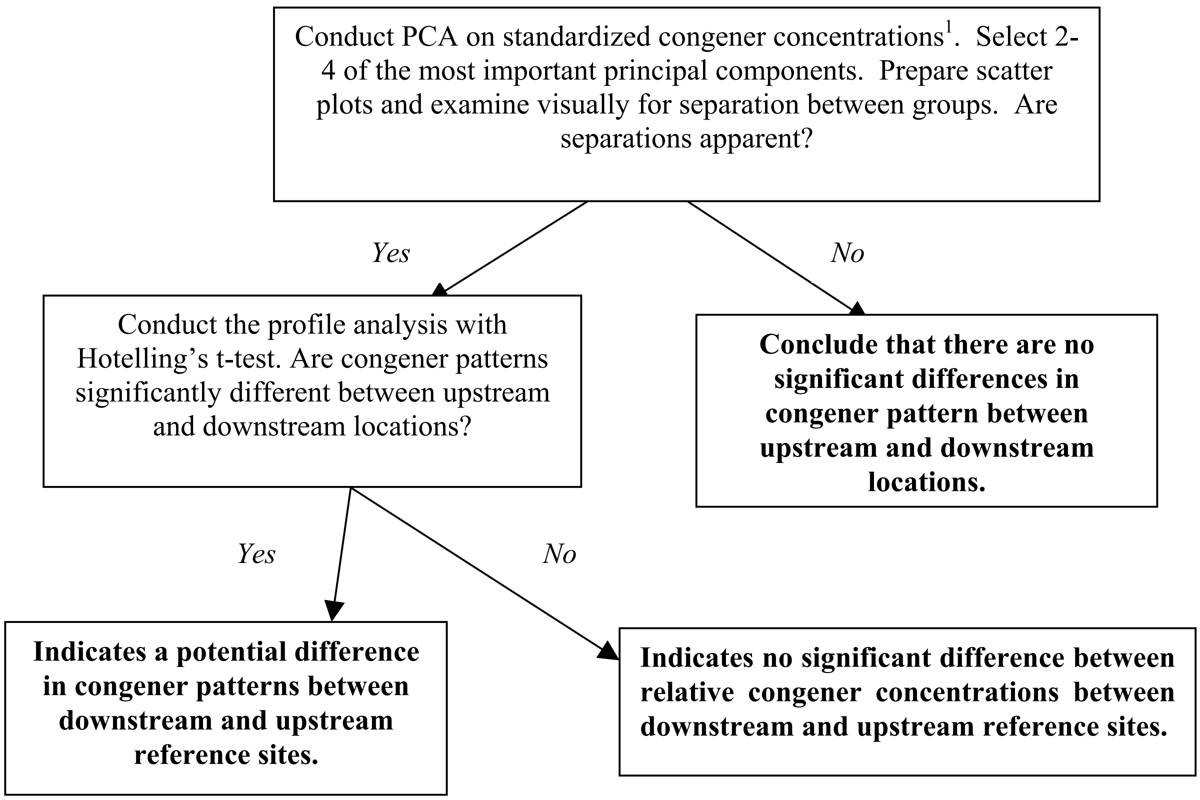


Figure 6-4. Flowchart for pattern analysis in white-tailed deer, wild turkey, and rabbits.

[1] These multivariate statistical procedures use individual congener concentrations measured in samples collected from each location and sample type, but individual congener concentrations will not be compared among locations.

7.0 REFERENCES

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Appendix B. Quality Assurance Project Plan (QAPP)

DRAFT

DRAFT QUALITY ASSURANCE PROJECT PLAN FOR ANALYSIS ASSOCIATED WITH THE INTERIM RESPONSE ACTIVITY OF EVALUATING WILD GAME TAKEN FROM THE TITTABAWASSEE RIVER FLOODPLAIN

Prepared by:
ENTRIX, Inc.
East Lansing, Michigan

Prepared for:
The Dow Chemical Company
Midland, Michigan

November 2003

APPROVAL PAGE

Approved by: ______________________________ Date: ______________
[ENTRIX, Inc. Project Director]

Approved by: ______________________________ Date: ______________
[Client Project Manager]

Approved by: ______________________________ Date: ______________
[Quality Assurance Manager]

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Definitions and Acronyms

95% UCL	95-percent upper confidence limit
ASTM	American Society for Testing and Materials
COC	Chain-of-custody
CUR	Condition upon receipt report
DQO	Data quality objective
Dup	Duplicate
EDD	Electronic data deliverable
ERB	Equipment rinsate blank
FTL	Field team leader
GC	Gas chromatograph
GIS	Geographic Information Systems
HASP	Health and safety plan
IDL	Instrument detection limit
LCS	Laboratory control samples
MCL	Maximum contaminant levels
MDEQ	Michigan Department of Environmental Quality
MDL	Method detection limit
µg	Microgram
mg	Milligram
mL	Milliliter
MS	Mass spectrometer
MS/MSD	Matrix spike/matrix spike duplicate
NIST	National Institute of Standards and Technology
PARCCS	Precision accuracy representativeness comparability completeness sensitivity
PCBs	Polychlorinated biphenyls
PCDD/F	Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans
QA	Quality assurance
QAMP	Quality assurance management plan
QAPP	Quality Assurance Project Plan
QC	Quality control
RL	Reporting limit
RPD	Relative percent difference
RRT	Record retention time
SDG	Sample delivery group
SOP	Standard operating procedure
SRM	Standard reference material
SSO	Site safety officer
TAL	Target analyte list
USEPA	United States Environmental Protection Agency

1.0 INTRODUCTION

The purpose of this document is to present the quality assurance/quality control (QA/QC) requirements for the investigations described herein. This Quality Assurance Project Plan (QAPP) has been prepared in accordance with the guidance manuals "EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations" (EPA QA/R-5) (USEPA, 1994a), "Guidance for Quality Assurance Project Plans" (EPA QA/G-5) (USEPA 1998), and "Guidance for the Data Quality Objectives Process" (EPA QA/G-4) (USEPA, 1994b).

To provide a consistent framework, the format of this document closely follows the specifications and instructions for information as presented in EPA QA/R-5. EPA QA/R-5 identifies four elements that must be addressed in a QAPP. The four elements (termed "groups") and their locations in this document are as follows:

- **Group A, Project Management.** A discussion of this element can be found in Section 2.0 of the QAPP. The objective of this section is to provide an overview of project management, including project history and objectives, roles and responsibilities.
- **Group B, Measurement/Data Acquisition.** This element is presented in Section 3.0 of the QAPP. This section covers all aspects of measurement systems design and implementation.
- **Group C, Assessment/Oversight.** This element addresses the activities associated with assessing the effectiveness of the implementation of the project and associated QA/QC. It is discussed in Section 4.0 of the QAPP.
- **Group D, Data Validation and Usability.** Section 5.0 of the QAPP discusses this element. It covers the QA activities that occur after the data collection phase of the project is completed.

2.0 PROJECT MANAGEMENT

This section provides the overall approach to managing the investigations and addresses the following:

- Project organization and roles and responsibilities.
- Problem definition.
- Problem description.
- Project Data Quality Objectives (DQOs) and criteria for measurement data.
- Special training requirements or certificates required for work performed.
- Documentation and records management.

2.1 Project Organization and Roles and Responsibilities

This section contains descriptions of the project roles and responsibilities for the principal project team members. Figure 2-1 presents the project organization chart.

Project Manager — Dr. Alan Blankenship will oversee and approve all project activities; review QA reports; approve final project QA needs; authorize necessary actions and adjustments to accomplish program QA objectives; and act as liaison between agencies, field staff, and the CLIENT Project Manager.

Quality Assurance (QA) Auditor — (To Be Named) An independent advisor will review all QA activities to ensure compliance with contract specifications. The auditor will review all data deliverables to ensure data quality and usability. The identity of this person or persons will be determined by discussion among the involved stakeholders.

Quality Assurance (QA) Manager – Dr. Paul Jones will initiate audits on work completed by project personnel and subcontractors, including analytical laboratories and independent data validation contractors. The manager will review program QA activities, quality problems, and quality-related requests. In response to field and analytical findings, the QA manager will approve corrective actions. The QA manager will report quality non-conformances to the Project Manager and review all pertinent portions of the deliverables before they are transmitted to ensure conformance with QA/QC procedures and quality work product.

Field Team Leader (FTL) — Mr. Patrick Bradley will oversee field activities and supervise the field crews. The FTL will ensure that proper sample collection, preservation, storage, transport, and COC QC procedures are followed will inform the Project QA Manager when field problems occur, and will communicate and document corrective actions taken. The FTL will discuss field activities with the Project Manager.

Laboratory Project Manager — (To be determined) This person is responsible for assuring that the analysis of all samples submitted to ENTRIX, Inc. is performed in accordance with the QAPP and the laboratory's quality assurance manual. The Laboratory Project Manager is the liaison between the laboratory staff and is responsible for keeping the project director and the laboratory informed of project status. In addition, the Laboratory Project Manager performs the final laboratory review of project data packages for completeness and compliance with project requirements.

Project Coordinator/Data Manager – Dr. Denise Kay will coordinate Entrix activities on the project. These will include data and documentation preparation and dissemination. She will be responsible for the structure, organization, format, implementation, and operation of the study plan databases. A central project database will be constructed using object linking and embedding by accessing the individual study plan databases. She will also be responsible for preparation of data deliverables.

Data Interpretation – Dr. Alan Blankenship will be responsible for compilation of summary results and project final reports. He will also be responsible for statistical analysis of results.

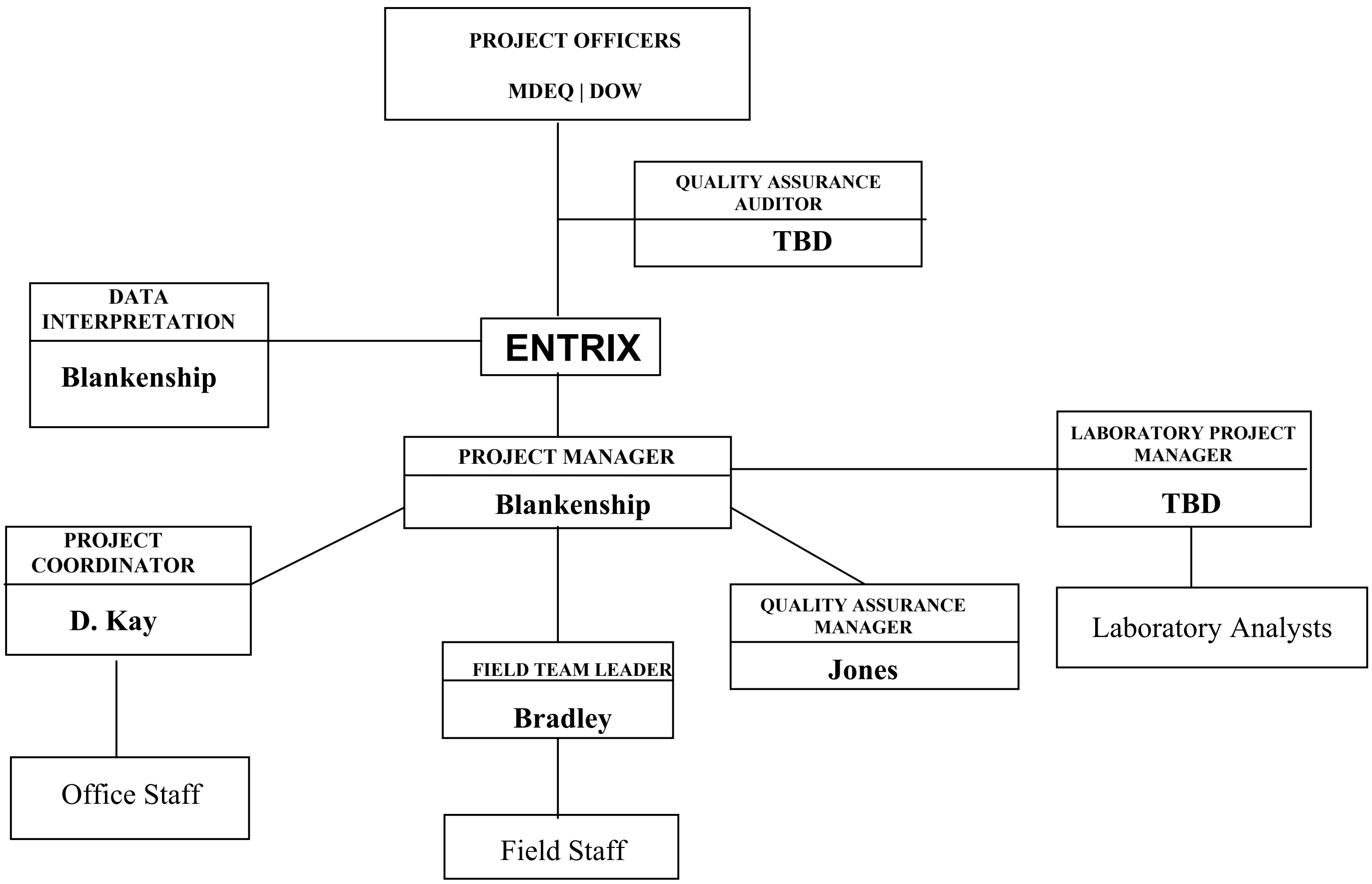

Figure 2-1. Project Organizational Chart

2.2 Problem Definition

The wild game sampling effort is designed to provide a survey of tissue residue concentrations in wild game that are potentially exposed to PCDD/Fs in the Tittabawassee River floodplain soils. The results from this field sampling will be used to help determine the potential human exposure pathway to PCDD/Fs via consumption of wild game from the Tittabawassee floodplain.

2.3 Project Description

The purpose of the wild game sampling effort is: (1) to gain a better understanding of the concentrations of PCDD/Fs in edible tissue from wild game animals collected from locations upstream and downstream of Midland, Michigan and (2) to evaluate the potential human exposure pathway of PCDD/F via consumption of these wild game animals. The following wild game animals will be the focus of this investigation:

- White-tailed deer
- Wild turkey
- Squirrels and/or Rabbits

2.3.1 Applicable Technical Quality Standards or Criteria

The study is being conducted to evaluate PCDD/Fs exposure to humans through consumption of wild game animals. As such, there are no applicable regulatory or technical standards to which the analytical data will be compared.

2.3.2 Special Personnel or Equipment Requirements

Special personnel for the proposed work include sharpshooters from the Wildlife Division of the United States Department of Agriculture (USDA) or their designee. These persons will be responsible for hunting all specimens of deer, turkey, and small mammals. Procedures and necessary equipment for the collection of wild game animals are specified in SOPs 229, 230, and 231 (Appendix C of the Wild Game Work Plan).

2.3.3 Assessment Techniques

A summary of assessment activities that are required for the work are as follows:

- Assessment of field operations. To evaluate field operations performance, frequent review of documentation, COCs, field notebooks and field measurement will be conducted.
- Assessment of laboratory operations. Any nonconformities in the laboratory will be reported to the Laboratory Manager and the Project Director, and official notification of corrective actions will be reported to the QA Manager and Project Director within an additional five working days. If the QA Manager determines that nonconformities are of a nature that would compromise sample integrity he will have authority to order immediate cessation of laboratory operations until corrective measures are in place and notified to the QA manager and Project Director.

Specific details of assessment procedures can be found in Section 4.0.

2.3.4 Work Schedule

Upon approval of the preliminary Work Plan and collection permits, fieldwork is scheduled to be completed within 6 weeks. Sample analysis will be completed by the end of March 2004.

2.3.5 Project and Quality Records and Reports

Critical records for this project include:

- field operations records;
- project reports outlined above; and
- laboratory records.

More details on project records and reports can be found in Section 2.6.

2.4 Data Quality Objectives and Criteria for Measurement Data

In this section the data quality objectives for the work tasks and the performance criteria and measurement system that will be employed are discussed.

2.4.1 DQO Development

Data quality objectives (DQOs) are both qualitative and quantitative statements that define the type, quality, and quantity of environmental data appropriate for the intended application. The DQO process used for this project follows the EPA QA/R-5 regulations (USEPA 1998) and EPA QA/G-4 guidance (USEPA 1994b). Quality assurance activities associated with wild game sampling tasks are addressed in the SOPs for those activities.

2.4.2 Method Performance Objectives

The sampling approach and rationale are presented in the Work Plan and discussed in terms of DQOs. Method performance requirements for analytical laboratory methods to be performed for the study are expressed in terms of precision, accuracy, representativeness, comparability, completeness, and sensitivity (PARCCS). Summarized below are brief definitions for each PARCCS parameter, with calculation equations as appropriate.

2.4.2.1 Precision

Precision is an estimate of the variability between individual measurements of the same physical or chemical property, under prescribed similar conditions.

<u>Field Precision</u>

Field precision is usually assessed through the collection and measurement of duplicate field samples at the same location. The duplicate sample is submitted “blind” to the laboratory, and sample results are compared to check for the overall variability introduced by sampling and analytical procedures. However, this approach is not generally useful for solid matrices such as tissue due their inherent variability, which precludes obtaining a true duplicate. Therefore, field duplicates of tissue samples will not be collected for this study.

<u>Laboratory Precision</u>

Precision in the laboratory is assessed through the calculation of the relative percent difference (RPD) for two replicate samples. The precision of the analysis can be inferred through the use of one of the following: 1) laboratory control spike and laboratory control spike duplicate (LCS and LCSD) samples, which are laboratory blank samples spiked with known analyte concentrations, 2) matrix spike and matrix spike duplicate (MS/MSD) samples which are project samples spiked with known analyte concentrations, or 3) duplicate analyses of unspiked project samples. The laboratory analyzes one or more of the aforementioned types of duplicate samples at a rate of one per batch of twenty (20) or fewer investigative samples per matrix.

The MS/MSD samples provide information about the effect of the sample matrix on extraction and measurement methodology. An MS/MSD pair will be analyzed at a rate of one per twenty (20) per analytical batch or fewer investigative samples per matrix.

Calculating the RPD for each pair of duplicate analyses (e.g., MS/MSD, laboratory control sample spike duplicates, unspiked duplicate samples) and the RPD for field duplicate sets, using the following formula will assess the precision of laboratory analyses:

Equation 2-1

$$RPD = \frac{S - D}{(S + D)/2} x100$$

where:

RPD	=	Relative Percent Difference, %.
S	=	First sample value (original or MS value or larger of the duplicate),
D	=	Second sample value (duplicate or MSD value or smaller of the duplicate),

2.4.2.2 Accuracy

Accuracy is the degree of agreement between a measurement or observation and an accepted value.

Field Accuracy

Accuracy in the field is assessed through the collection and analysis of appropriate field equipment blanks and trip blanks, and achieved through adherence to all sample handling, preservation, and holding time requirements. Field blank samples are analyzed to check for procedural contamination that may cause sample contamination. Equipment rinse blanks are used to assess the adequacy of decontamination of sampling equipment between collection of individual samples. Trip blanks are used to assess the potential for contamination of samples due to contaminant (i.e., volatile organic compounds) migration during sample shipment, handling, and storage. Accuracy of the field instruments will be assessed by using daily instrument calibration and calibration checks. Field blank, equipment rinsate blank, and trip blank analysis frequencies are given in Table 2-1.

Laboratory Accuracy

Laboratory accuracy is assessed by the analysis of method blanks, surrogate spikes, matrix spikes (MS), laboratory control samples (LCS), and/or Standard/Certified Reference Materials (SRM). The results are expressed as percent recovery. Method blank samples are generated within the laboratory and used to assess contamination resulting from laboratory procedures. Surrogate compounds are used in analyses for organic contaminants and specified in the analytical method. Prior to sample extraction, surrogate compounds are added to each organic environmental, blank, spike, and duplicate sample. Method blanks, MS, LCS, and/or SRM samples will be analyzed at a rate of one per analytical batch of twenty (20) or fewer investigative samples/matrix.

The percent recovery (percent R) of spike samples will be calculated using the formula:

Equation 2-2

$$R = \frac{A - B}{C} x100$$

where:

R = Recovery, %

A = The analyte concentration determined experimentally from the spiked sample, units.

B = The background level determined by a separate analysis of the unspiked sample, units.

C = The amount of the spike added, units.

Table 2-1. Field QC Samples for Precision and Accuracy.

Type of QC Sample	Frequency	Acceptance Criteria
Equipment rinsate blank	2 per day per equipment type	No analyte should be detected at >3 times the laboratory blank
Matrix spike/matrix spike duplicate (MS/MSD)	1 per 20 tissue samples	RPD should be ≤30 % for each analyte.
Field blank	1 per day	No analyte should be detected at >3 times the laboratory blank.

Note: MS/MSD samples are included as field QC samples for planning purposes, to ensure sufficient sample volume is collected for the analyses.

2.4.2.3 Representativeness

Representativeness is a qualitative measure of the degree to which sample data accurately and precisely represent a characteristic environmental condition. Representativeness is a subjective parameter and is used to evaluate the efficacy of the sampling plan design. Representativeness is demonstrated by providing full descriptions of the sampling techniques and the rationale used for selecting certain tissue samples and sampling locations in the project planning documents.

There cannot be a target numerical goal for a qualitative parameter such as representativeness or comparability. Therefore, this criterion is completed and evaluated subjectively rather than quantitatively. The measure for representativeness is answered during the preparation of the sampling and analysis approach and rationale, and then reassessed during the data usability process. For example, an integral part of developing the sampling and analysis approach and rationale is to answer the question "How many samples are needed to fully evaluate x?" Then, during the data usability process, the question "Were enough data collected to answer the original question?" must be answered. Thus, it is not possible to construct a table with numerical goals that can be used to evaluate these subjective measures.

Since the analytical samples will be obtained as homogenized tissue composites from individual specimens an assessment of the representativeness of the homogenized samples is required. Deer and turkey homogenates will be prepared as composite samples containing standardized amounts of collected muscle tissue. Muscle tissue from the rump, tenderloin and back strap will be collected from deer and muscle tissue from the breast and legs will be collected from turkeys (see Work Plan and SOPs 230 and 231 for details). To ensure complete homogenization of the samples, duplicate aliquots of 10% of samples will be submitted to the analytical laboratories as blind replicates.

2.4.2.4 Comparability

Comparability expresses the confidence with which one data set can be compared with another data set obtained during parallel or previous investigations. Comparability can be related to precision and accuracy, as these parameters are measures of data reliability.

Chemical samples from the same medium are generally considered comparable if the same procedures for collecting and analyzing the samples are employed, if the samples comply with the same QA/QC procedures, and if the units of measurements are the same.

The tissue types to be collected for analysis for this study have not been collected from the Tittabawassee River previously. Therefore, wild game tissue samples will not be comparable with previous tissue collections from the site.

The analytical protocols for PCDD/F determination for this study will be comparable with previous data collected for fish in the river (Hilscherova et al. 2003). The method used, based on US-EPA method 8290, determines each PCDD/F congener individually so data will be amenable to comparison with other PCDD/F determinations. The acceptability criteria for the method are performance based on compliance with QA/QC requirements will be ensured.

The quality objective for data from each field sampling and analysis task within this study is to achieve a level of comparability that allows for the comparison of data collected among all field tasks for this study. To accomplish this goal, all data generated during the tasks included in this investigation will be subject to strict QA/QC procedures that are specified in this QAPP.

2.4.2.5 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was planned to be obtained under normal conditions. Data completeness will be calculated by using Equation 2-3.

<u>Equation 2-3</u>

$$\%\ \text{Completeness} = \frac{\text{Valid Data Obtained}}{\text{Total Data Planned}} \text{x}100$$

Experience on similar projects has shown a reasonable goal considering combined historical field and laboratory performance is 90 percent completeness. All valid data will be used. During the data validation process, an assessment will be made of whether the valid data are sufficient to meet project objectives. If sufficient valid data are not obtained, the Project Manager will initiate corrective action.

2.4.2.6 Sensitivity

Sensitivity is the measure of the concentration at which an analytical method can positively identify and report analytical results. The sensitivity of a given method is commonly referred to as the detection limit. Although there is no single definition of this term, the following terms and definitions of detection limits will be used for this program.

- **Instrument detection limit** (IDL) is the minimum mass of analyte that can be measured above instrument background noise under ideal conditions.
- **Method detection limit** (MDL) is a statistically determined concentration. It is the minimum concentration of an analyte that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero as determined in the same or a similar matrix. MDL shall be determined as described in EPA methods 8290 and 1613.

The sum TEQ for all MDLs in a single sample may not exceed 0.9 TEQ. Table 2-2 gives target ranges for congener specific MDLs. These limits are of sufficient sensitivity to allow for comparison to toxicological benchmarks. The MDL for each congener is a function of signal to noise ratio for each sample, which affects the amount of compound detectably different from baseline, and the sample mass used. An MDL is also provided based on the calculation of "total dioxin equivalents" based on the WHO promulgated TEF values for humans (Van Den Berg et al. 1998).

Sample MDLs will vary from sample to sample and will depend on the amount of samples processed. Failure of the analytical laboratories to achieve the required MDLs will impair the ability to statistically compare sampling locations.

Table 2-2. PCDD/F Congeners to be analyzed and target MDLs

Compound	CAS No	Target MDL (pg/g)*
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	1746-01-6	0.1-1
1,2,3,7,8-Pentachlorodibenzo-p-dioxin (PeCDD)	40321-76-4	0.1-1
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	57653-85-7	0.1-1
1,2,3,4,7,8- Hexachlorodibenzo-p-dioxin (HxCDD)	39227-28-6	0.1-1
1,2,3,7,8,9- Hexachlorodibenzo-p-dioxin (HxCDD)	19408-74-3	0.1-1
1,2,3,4,6,7,8- Heptachlorodibenzo-p-dioxin (HpCDD)	35822-39-4	0.1-1
Octachlorodibenzo-p-dioxin (OCDD)	3268-87-9	1-5
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	51207-31-9	0.1-1
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	57117-41-6	0.1-1
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	57117-31-4	0.1-1
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	57117-44-9	0.1-1
1,2,3,7,8,9- Hexachlorodibenzofuran (HxCDF)	72918-21-9	0.1-1
1,2,3,4,7,8- Hexachlorodibenzofuran (HxCDF)	70648-26-9	0.1-1
2,3,4,6,7,8- Hexachlorodibenzofuran (HxCDF)	60851-34-5	0.1-1
1,2,3,4,6,7,8- Heptachlorodibenzofuran (HpCDF)	67562-39-4	0.1-1
1,2,3,4,7,8,9- Heptachlorodibenzofuran (HpCDF)	55673-89-7	0.1-1
Octachlorodibenzofuran (OCDF)	39001-02-0	0.1-1
SUM WHO-TEQ MUST NOT EXCEED 0.9		

* Units represent wet wt for tissues.

2.5 Laboratory Comparison

To ensure timely, accurate and independently verifiable results for this study, two primary analytical facilities have been selected (see Section 3.1.2). To ensure the validity and comparability of results from the two laboratories, a program of blind sample replicates will be used to provide data for intra- and inter-laboratory comparison. An initial set of 20-30 samples, including blind replicates, will be submitted to each laboratory.

The allocation of the remaining samples to the two laboratories will be based on:

- Turn-around time achieved.
- Detection limits achieved.
- Blind sample replicate performance.
- Data “suitability for use”.
- Adequacy of reporting.

Quality assurance criteria for acceptability and usability of data are provided in Table 3-4 of this QAPP.

2.6 Special Training, Requirements, and Certifications

The Project Manager is responsible for assembling a project team with the necessary experience and technical skills. Part of the process is to identify special training requirements or certifications necessary to execute the project successfully. Project-specific requirements include training specific to the analytical methods to be conducted, specific collection and handling methods for tissue samples, and health and safety training for field and laboratory activities.

All ENTRIX field personnel will receive training before commencing fieldwork to ensure they are familiar with the required SOPs and are adequately skilled at sample and field data collection. Personnel training records are maintained at the ENTRIX office by the office staff.

Additionally, all contractors working at the site should have the appropriate health and safety training as outlined in the Health and Safety Plan.

The analytical laboratories chosen for the study both have extensive experience and certification for the determination of PCDD/Fs in a wide variety of matrices. Both laboratories are recognized as world leaders in this field of analysis.

2.7 Documentation and Records

This section identifies critical field and laboratory records required for this project, information to be included in project reports, the data reporting format for analytical data report packages, and the document control procedures to be used.

2.7.1 Required Records

The critical records required for this project are identified below with descriptive or supporting information as appropriate. Records information is presented below for field operations. Critical laboratory records are described in Section 2.7.3 of this QAPP.

Critical records generated during field operations are listed below.

- Sample collection records including field notebooks, photographs, and any other records used to record raw data. General field procedures will be referenced in the field notes, while any necessary deviations or modifications required to collect samples will be described in detail.
- Chain-of-custody records (COC).
- Field QC sample records.
- Corrective action reports.

The information contained in these records documents the overall field operations. Procedures for field operations records control, archiving, and storage are described in Section 2.7.4 of this QAPP.

2.7.2 Project Reports

Several types of reports will be produced during the course of this project. The Project Manager will prepare summary reports for investigations described herein. Tasks described herein will be submitted in the following technical report publications and manuscripts to be submitted to the peer-reviewed scientific literature, including summary report of data and QA determinations.

2.7.3 Laboratory Records

All analytical results for tissue data will be reported in an approved format, described below. In addition to the reported data, the laboratory data report will, at a minimum, include a narrative that will discuss any problems or discrepancies, and sufficient calibration and QC information to determine that the method was in control at the time that the samples were analyzed. The laboratory records will include:

- Case narrative;
- COC documentation (external);

- Laboratory sample ID, field sample ID, location, matrix, and dilution factors;
- Sample receipt, extraction, and analysis dates for holding time verification;
- Percent recovery of each surrogate;
- Final analyte concentration including reporting limit, laboratory qualifiers, and re-analyses;
- Surrogate recovery control limits;
- Percent recovery of each compound in the MS sample;
- MS recovery control limits;
- RPD for all MS/MSD and/or LCS/LCSD results;
- RPD control limits for MS/MSD and/or LCS/LCSD reports;
- Laboratory control sample results when analyzed;
- Recovery control limits for LCS or SRM recoveries and RSD;
- Blank results for method blanks, field blanks, equipment blanks, and trip blanks; and
- Method blank summary indicating associated samples.

For data validation, the following additional data will be required:

- Sample receipt/sample log-in forms;
- Calibration information, including initial calibration, concentration response data of the calibration check standards, continuing calibration check data, instrument tunes, and associated samples;
- Internal standard areas and retention times; and
- All raw data and logs will include the following information:
    - analyst's initials and date
    - initial and final sample and extract volumes or weights and/or dilutions
    - condition of instrument (e.g., retention times for GC)
    - documentation linking sample analysis to instrument calibration (where appropriate)
    - time of start of analysis of all field and QC samples
    - instrument run log showing analytical sequence
    - dilutions performed and amount of sample analyzed or injected
    - field samples, QC samples, and blanks clearly labeled
    - chromatograms and quantitation reports
    - sample preservation (where applicable)

In addition to the hard-copy report requirements, the laboratory will provide (1) electronic deliverables conforming to an ASCII comma-delimited format for all data reported and (2) an electronic back up for all laboratory data generated.

Procedures for project control, archiving, and storage of laboratory records are described in Section 2.6.4 of this QAPP. The laboratory's internal records management protocols are described in SOP #802 entitled, "Data Package Review". A copy of SOP #802 is included as an appendix to the Wild Game Work Plan (Appendix D). ENTRIX, Inc. will adhere to a record retention time (RRT) of 7 years for all laboratory records for the project.

2.7.4 Record Maintenance and Storage

All documents relating to the project will be controlled to assure proper distribution, filing, and retrieval, and to assure that revisions are properly recorded, distributed, and filed.

Project records will be stored and maintained by ENTRIX, Inc. The Project Manager and office staff are responsible for organizing, storing, and cataloging all project information and for collecting records and supporting data from project team members. Once cataloged, ENTRIX will assure that project records are appropriately filed by category in the correct project file. Filed documents are available to ENTRIX staff through check-out procedures developed to assure the integrity of the project file. Individual project team members may maintain separate files or notebooks for individual tasks. These files or notebooks are transferred to the project manager as part of project close-out. The archived files will be stored and maintained by ENTRIX, Inc. Additional information on record management can be found in Section 3.9.7 and 3.9.8 of this QAPP.

3.0 MEASUREMENT AND DATA ACQUISITION

This section describes all aspects of measurement design and implementation, and discusses the methods that will be used for sampling, analysis, data handling, and QC in support of the tasks discussed herein. The following specific aspects of measurement and data acquisition will be covered in this section:

- Sampling process design;
- Sampling methods requirements;
- Sample handling and custody requirements;
- Analytical method requirements;
- Quality control requirements;
- Instrument/equipment testing, inspection, and maintenance requirements;
- Instrument calibration and frequency;
- Inspection and acceptance requirements for supplies and consumables;
- Data acquisition requirements; and
- Data management.

3.1 Sampling Process Design

The measurements to be taken and the media to be sampled include concentrations of PCDD/F congeners in various tissues of wild game animals.

The planned sampling locations and rationale for selection are detailed in the Work Plan. Any modifications to the work tasks described therein will be presented as an addendum or update to the Work Plan.

3.1.1 Field Sampling Documentation

ENTRIX field team members will maintain bound field logbooks to provide a daily record of significant events, observations, and measurements during sampling. Each data book will have a unique identifier and each page and carbon copy will include this data book identifier. All information pertinent to sampling will be recorded in the logbooks. Each day's logbook entries will be signed and dated and will include:

- Name and title of author, date and time of entry, and weather and environmental conditions during the field activity;
- Location of sampling activity;
- Sampled species (e.g., white-tailed deer, wild turkey, or rabbit);
- Sample collection method (e.g. shotgun,); and
- Number of samples taken.

When activity-specific data forms are used, they will also include:

- Project name and number;
- Investigation location;
- Sampler's initials;
- Sampled species; and
- Sample collection method.

The following information will be recorded either in the logbook or on the activity-specific data forms:

- Date and time of collection;
- Sample identification number(s);
- Sample destination (e.g., laboratory);
- Field observations;
- Field measurements; and
- Sample handling (preservation).

All original data recorded in field logbooks, field data forms, sample labels, and COC forms must be written with waterproof, indelible ink. None of these accountable, serialized documents are to be destroyed or discarded, even if one is illegible or contains inaccuracies requiring document replacement. If an error is made on an accountable document assigned to one individual, that individual will make all corrections simply by crossing a line through the error, initialing and dating the correction, and entering the correct information. The erroneous information will not be obliterated. The person who made the entry will correct any subsequent error discovered on an accountable document. All personnel will be trained in the proper use of notebooks during training for field work.

3.1.2 Sample Identification

The field analysis and sample identity information are recorded in bound field logbooks or recorded on data sheets while in the custody of the sampling team.

A sample label will be completed and attached to each animal and sample container for every species collected. Labels consist of a waterproof material backed with a water-resistant adhesive. Labels are to be filled out using waterproof ink, and are to contain at least the following information:

- Sampling date and time;
- Sample identification number;
- Investigation location;
- Sampler's initials;
- Sample matrix or matrix identifier.

Each analytical sample will be assigned a unique number consisting of an alphanumeric code that identifies the investigative area, medium (tissue), and the specific sampling location. These numbers will be tracked electronically, from collection through laboratory analysis and into the final reports.

The sample number will be cross-referenced with the site name and sample location on the COC. Additional sample volume will be collected for samples identified by ENTRIX for laboratory QC (i.e., MS, MSD, DUP) and identified as "For Lab QC Use." Information to be included on COCs is specified in SOP #401 entitled, "Sample Management - Receiving, Preservation, Storage, Documentation, Decontamination, and Disposal".

3.1.2.1 Tissue Sample Handling Procedures

Appropriate sample containers will be sealed, labeled, and placed on wet or blue ice in an insulated container. Appropriate COC documentation will accompany the samples as required by the QAPP. Specific sample volumes, sample containers, preservatives, and replication of samples are detailed in the following sections. Any sampling equipment that will be reused will be decontaminated by rinsing with deionized water followed by reagent grade acetone and hexane between sampling.

3.1.2.2 Decontamination Procedures and Materials

All equipment used during investigation activities that could come into contact with chemically affected materials will be thoroughly cleaned, before and after each use, by washing with Liquinox (a laboratory-grade detergent) and rinsing with deionized water followed by reagent grade acetone and hexane. Decontamination procedures may be modified and/or revised based upon the data obtained or the field equipment used.

Decontamination waste is expected to consist of acetone and hexane. Decontamination solutions will first be discharged to drums in a designated staging area and then later transferred to laboratory facilities for proper disposal and management.

3.1.3 Support Facilities for Sampling Methods

The primary laboratories for analysis of samples collected for this study will be:

AgriQuality Limited, 1B Bell Road, PO Box 31-242, Lower Hutt, New Zealand.

ALTA Analytical Laboratory, 1104 Windfield Way, El Dorado Hills, CA 95762.

3.1.4 Sampling/Measurement Failure Response

If QC surveillance and/or field audits result in detection of unacceptable conditions, procedures or data, the Project Manager, in conjunction with the QA Manager, will be responsible for developing and directing implementation of corrective actions. Corrective actions will include one or more of the following:

- Identifying the root cause of the problem and implementing systems to prevent future occurrences;
- Identifying the source of the violation;
- Evaluating and amending sampling and/or analytical procedures; and
- Accepting data and flagging the data to indicate the level of uncertainty associated with failure to meet the specified QC performance criteria.

Any finding requiring corrective action must be documented to the Project Manager. The Project QA Manager will check to ensure that corrective actions have been implemented and that the problem has been resolved. Problems will be addressed and the corrective action noted in the appropriate lab or field notebook.

If an error is made on an accountable document assigned to one individual, that individual will make all corrections simply by crossing a line through the error, initialing and dating the correction, and entering the correct information. The erroneous information will not be obliterated. The person who made the entry will correct any subsequent error discovered on an accountable document.

3.1.5 Sample Preservation and Holding Time Requirements

The sample containers, preservative requirements, and maximum holding times for analytical methods used in this project are provided in Table 3-1.

Table 3-1. Required Sample Containers, Preservation, and Holding Times.

Analyses	Sample Matrix[a]	Container[b]	Preservative[c]	Holding Time[d]
PCDD/F congeners (EPA Method 8290)	T	125ml Glass	Freeze -20°C	180 days
PCB Congeners (EPA Method 8290)	T	125ml Glass	Freeze -20°C	180 days
Percent Lipids (gravimetric)	T	N/A	Freeze -20°C	NA

Note:
Sample container and volume requirements will be specified by the analytical laboratory performing the tests. Three times the required volume should be collected for samples designated as MS/MSD samples.

[a] Sample matrix: T = Tissue

[b] Glass containers will be pre-cleaned and sealed with Teflon®-lined screw caps and solvent rinsed foil.

[c] Tissue samples will be shipped at 4°C to the laboratory and stored at -20°C after dissection/processing.

[d] Holding times are from the time of sample collection. Holding times are based on method 8290. All extracts will be analyzed within 45 days of extraction. Numbers represent days to analysis of extract.

3.2 Sample Handling and Chain of Custody Requirements

Proper sample handling, shipment, and maintenance of chain of custody (COC) are key components of building the documentation and support for data that can be used to make program decisions. It is essential that all sample handling and sample COC requirements be performed in a complete, accurate, and consistent manner. Sample handling and custody requirements must be followed for all samples collected as part of this project.

3.2.1 Sample Custody

Sample custody and documentation procedures described herein must be followed throughout all sample collection activities. Components of sample custody procedures include the use of field logbooks, sample labels, custody seals, and COC forms. The COC form must accompany the samples during shipment from the field to the laboratory.

A sample is under custody under the following conditions:

- It is in one's actual possession;
- It is in one's view, after being in his or her physical possession;
- It was in one's physical possession and that person then locked it up to prevent tampering; and/or
- It is in a designated and identified secure area.

The following procedures must be used to document, establish, and maintain custody of field samples:

- A sample label will be completed and attached to each sample container for every sample collected. Labels consist of a waterproof material backed with a water-resistant adhesive. Labels are to be filled out using waterproof ink, making sure that the labels are legible and affixed firmly on the sample container. Sample labels are to contain at least the following information: sampling date and time; sample identification number; investigation location; and sampler's initials.
- All sample-related information must be recorded in the project logbook or on activity-specific data forms.
- The field sampler must retain custody of samples until they are transferred or properly dispatched.
- To simplify the COC record and minimize potential problems, as few people as possible should handle the samples or physical evidence. For this reason, one individual from the field sampling team should be designated as the responsible individual for all sample transfer activities. This field investigator will be responsible for the care and custody of the samples until they are properly transferred to another person or facility.
- A COC record will accompany all samples. This record documents the transfer of custody of samples from the field investigator to another person, to the laboratory, or other organizational entities, as a signature for relinquishment and receipt of the samples must accompany each change of possession. Chain-of-custody will be prepared for groups of samples collected at a given location on a given day.
- The COC form makes provision for documenting sample integrity and the identity of any persons involved in sample transfer. Information entered on the COC will consist of the following:
    - project name and number;
    - field logbook number;
    - chain-of-custody serial number;
    - project location;
    - sample numbers;
    - sampler/recorder's signature;
    - date and time of collection of each sample;
    - collection location;
    - sample type;
    - analyses requested;
    - inclusive dates of possession;
    - name of person receiving the sample;
    - laboratory sample number;
    - date of receipt of sample;

  - name, address, and telephone number of laboratory;
  - name, address, and telephone number of person to whom laboratory report will be sent; and
  - method of delivery and courier.
- Completed COC forms will be inserted into a Ziploc™ bag, sealed, and taped to the inside cover of the shipping container used for sample transport from the field to the laboratory when a courier or shipping company is used. The shipping company will not sign for custody of the samples.
- When samples are relinquished to a courier for transport, the tracking number from the shipping bill or receipt will be recorded on the COC form or in the site logbook.
- The recipient for the samples must be notified of the date of shipment and anticipated time of arrival. The shipping bill number must also be provided to the recipient to enable tracking of samples
- It must be clearly established prior to shipment who will be responsible for ensuring that timely sample delivery occurs and who will track the samples in case of shipping delays.
- The recipient of the samples must inform the sender when the samples are delivered.
- Custody seals must be affixed on shipping containers when samples are shipped to the laboratory to prevent sample tampering during transportation.
- In cases of delivery delay or packing damage all details of damage and sample condition must be recorded and if necessary photographed for documentation.

3.2.1.1 Laboratory Sample Handling and Custody

The Project Liaison or Field Team Leader (FTL) will notify the Laboratory Project Manager of upcoming field sampling activities and the subsequent transfer of samples to the laboratory. This notification will include information concerning the number and type of samples to be shipped, analyses requested, and the expected date of arrival. The Laboratory Project Manager will notify appropriate laboratory personnel about the expected shipment including the sample custodian.

Upon arrival at the laboratory, the samples will be received and logged in by a trained sample custodian in accordance with the laboratory's sample handling program. A description of the laboratory's general program is provided in SOP #401 and is summarized below.

Upon sample receipt, the sample custodian is responsible for performing the following activities during sample receipt where appropriate:

- Examining the shipping containers to verify custody tape is intact;
- Examining all sample containers for damage;
- Comparing samples received against those listed on the COC;
- Verifying sample holding times have not been exceeded;
- Determining sample temperature (from the temperature blank vial) and documenting variations from the acceptable range on the COC;
- Verifying that all samples listed on the COC are present or accounted for;

- Immediately signing and dating COC after shipment is accepted;
- Noting any sample receipt problems on the COC, initiating a Condition Upon Receipt report (CUR), and notifying the Laboratory Project Manager;
- Attaching laboratory sample container labels with laboratory identification number and test; and
- Placing the samples in proper laboratory storage.

The Laboratory Project Manager is responsible for contacting the Project Liaison as soon as possible if any problems are identified during sample receipt. All identified sample receiving problems will be resolved before sample preparation and analysis.

Following sample receipt, the sample custodian is responsible for logging the samples in the laboratory sample log-in book, and/or the Laboratory Information Management System (LIMS) with the following information:

- Laboratory project number;
- Sample numbers (laboratory and client);
- Type of samples;
- Required tests;
- Date collected; and
- Date received.

The sample custodian is also responsible for notifying the Laboratory Project Manager and appropriate Group/Team Leader(s) of sample arrival and placing completed COCs, waybills, and any additional documentation in the project file.

Samples will be stored appropriately within the laboratory to maintain any prescribed temperature, to protect against contamination, and to maintain the security of the samples.

If any samples are transferred to a different laboratory, the transfer will be done under COC procedures and ENTRIX will maintain the appropriate documentation to preserve the traceability of the samples through final analysis and disposal.

3.2.2 Sample Packing and Shipping

Samples will be delivered to the designated laboratories by field personnel, laboratory courier, or by commercial shipping services (such as UPS or Federal Express). The method of sample shipment will be noted on the COC. During the field effort, the FTL or a designee will inform the laboratory daily of planned shipments. Hard plastic ice chests or coolers with similar durability will be used for shipping samples. The coolers must be able to withstand a 4-foot drop onto solid concrete in the position most likely to cause damage. The samples will be packed to prevent the least amount of damage if such a fall would occur.

After packing is complete, the cooler will be taped shut with custody seals affixed across the top and bottom joints. Each container will be clearly marked with a sticker containing the originator's address.

The following procedures must be used when transferring samples for shipment.

- A COC form must accompany samples. When transferring possession of samples, the individuals relinquishing and receiving must sign, date, and note the time on the record. This record documents transfer of custody of samples from the field sampler to another person or to the laboratory. Overnight shipping companies will not be required to sign the COC. A copy of the receipt of shipment will accompany the COC.

- Samples must be properly packaged for shipment and dispatched to the appropriate laboratory for analysis with a separate signed COC form enclosed in each sample box or cooler. The COC should reflect only the contents of the cooler in which it is enclosed.
- A COC form identifying the contents must accompany all packages. The original record must accompany the shipment, and the FTL must retain a copy.

3.3 Analytical Methods Requirements

This subsection presents the analytical methods requirements for analyses that may be performed during the study including preparation/extraction procedures where appropriate and method performance requirements.

Agriquality and Alta will conduct laboratory analyses. The laboratory's QA protocols will be available in the project files and will contain summary information from the analytical methods including the following:

- Sample containers, preservatives, and holding times;
- Calibration requirements including frequency and acceptance criteria;
- Laboratory quality control samples including frequency, acceptance criteria, and corrective action; and
- MDLs.

More detailed information on the laboratory's analytical methods is presented in laboratory-specific SOPs that can be obtained directly from AgriQuality and Alta.

3.3.1 Analytical Methods

Analyses on this project will utilize EPA-approved methods, method 8290 or method 1613. Method references for laboratory analyses that may be performed are provided in Tables 3-2 including preparation/extraction methods where appropriate.

Table 3-2. Analytical Requirements for Tissue Methods.

Analyses	Preparatory Method	Analytical Method	Reference
PCDD/F congeners	Relevant SOPs	SW 846 (method 8290)	http://www.epa.gov/epaoswer/hazwaste/test/main.html
PCDD/F congeners	Relevant SOPs	Method 1613	CFR 62:48393-48442

3.3.2 Reporting Limits

Laboratory-specific MDLs for the analyses identified in Tables 3-2 and 3-3 are presented in Table 2-1. These MDLs are target values based on data quality requirements for the risk assessment of complex PCDD/F mixtures. These MDL may be modified based upon laboratory performance, sample matrix effects and/or changes to the methods. Any such modifications will be discussed with all stakeholders and any effects on the quality of subsequent risk assessment procedures will be determined.

3.3.3 Laboratory Method Performance Requirements

Summary tables of method-specific quality control samples that the laboratory uses to monitor method performance are provided in Tables 3-4 and 3-5. Acceptance criteria may be modified based upon the laboratory's current performance and/or changes to the methods. For each analysis, these tables present the types of QC samples to be run including the frequency, acceptance criteria and purpose of QC analysis. The laboratory analyst will review results of the quality control samples against the acceptance criteria. Any identified discrepancies will trigger the laboratory's internal corrective action system as described below.

Table 3-3. QC Samples and Acceptance Criteria for PCDD/F Congener Analysis

QA/QC Test	Acceptance Criteria	Frequency	Reason for Test
Retention time for Calibration Mix	value ±0.5min of mean	Daily	GC Performance
GC Linearity	PRRF CV ±3%	Weekly	Data Integrity
CRM/IRL	value ±20% of expected	1 per analytical set (20 samples)	Method Validation Representativeness and Comparability
Surrogate Recovery	value ±30% spiked concentration	for each sample extracted	Method Efficiency Data correction
Matrix Spike	value ±30% spiked concentration	1 per analytical set (20 samples)	Method Accuracy Representativeness and Comparability
Field Blank	concentration <IDL for first blank	1 per analytical set	Background Check; Complete Sampling System
Laboratory Blank	Should be < MDL, if present then MDL = concentration	1 per analytical set	Quality assurance (monitor laboratory contamination)
Field / Matrix spike Duplicate	RPD < 30%	1 per analytical set	Sampling Precision
Blind Check Sample	value ±30% expected value	Minimum of 1 during course of program	Method Validation; Representativeness and Comparability
Completeness	90% of Field Samples meet QA/QC	Evaluated at end of program	Project Integrity

3.3.4 Laboratory Corrective Action

Both laboratories have formal corrective action systems in place to assure that prompt action is taken when an unplanned deviation from a procedure or plan occurs and that whenever possible, corrective actions include measures to prevent the reoccurrence of deviations. Specific corrective actions will be taken and documented when a QC sample does not meet acceptance criteria. Following is a description of how information from the laboratory's corrective action system is communicated to the project team.

Corrective action procedures include prompt notification of the project contact (QA Manager) for any significant problems or discrepancies. The Laboratory Project Manager is responsible for reporting any significant problems or discrepancies that occur as analyses are conducted to the Project Liaison or other identified project contact. The Laboratory Project Manager is also responsible for assuring that corrective action is taken where appropriate to prevent the reoccurrence of similar problems or discrepancies. In addition, each analytical data report will include a case narrative that discusses any problems or discrepancies, and sufficient calibration and QC information to verify that the method was in control at the time that the samples were analyzed. The case narrative will also include a discussion of any corrective action taken by the laboratory to prevent the reoccurrence of similar problems or discrepancies.

3.4 Quality Control Requirements

This section presents the field QC checks that will be performed during field investigations including a discussion of field QC samples with frequency and acceptance criteria and field corrective action procedures. A discussion of laboratory QC samples is presented in Section 3.4.3 and laboratory corrective action is presented in Section 3.4.4.

3.4.1 Field QC Samples

The type and frequency of field QC samples to be collected during field investigations are summarized in Table 2-1 and are described below:

3.4.1.1 Equipment Rinsate Blank Samples

Equipment rinsate blanks (ERB) are samples of hexane passed through and over the surface of decontaminated sampling equipment. The rinsate is collected in sample bottles, preserved, and handled in the same manner as the samples. ERBs are used to monitor effectiveness of the decontamination process. The planned frequency for ERBs is one per day per equipment type. If more than one type of equipment is used to collect samples for a particular matrix, then an ERB is collected and submitted for each representative group of equipment. Typically, ERBs are analyzed for the same analytes as the corresponding samples collected that day.

3.4.1.2 Field (Trip) Blanks

Field blanks are unopened sample containers which are transported to and returned from the field collection location. Typically, at least one field blank per lot number of collected samples will be analyzed.

3.4.1.3 Duplicate (Blind) Field Samples

"Blind" duplicate field samples are collected to monitor the precision of the field sampling process. Tissue duplicates will not be available from field collections, however laboratory replicates will be submitted for analysis after tissue homogenization.

3.4.1.4 Independent Confirmation of Results

To permit validation of data determined by AgriQuality and Alta Analytical, sample splits will be provided to Dow Chemical. A section of the final report will provide a comparison of data derived at the three laboratories.

3.4.2 Field Corrective Action

Problems that require corrective action may be encountered in the field. Any finding requiring corrective action must be documented to the Project Manager. The Project QA Manager will check to ensure that corrective actions have been implemented and that the problem has been resolved. More easily addressed problems may also be encountered in the field. Such problems will be addressed and the corrective action noted in the appropriate field notebook. If an error is made on an accountable document assigned to one individual, that individual will make all corrections simply by crossing a line through the error, initialing and dating the correction, and entering the correct information. The erroneous information will not be obliterated. The person who made the entry will correct any subsequent error discovered on an accountable document.

3.5 Equipment Inspection, and Maintenance Requirements

Maintenance and inspection of both field and laboratory equipment are described in the following sections.

3.5.1 Field Instrument/Equipment

Preventative maintenance of field instrumentation and equipment will be performed according to manufacturer’s instructions. The field staff is responsible for ensuring that all instrumentation is operating properly prior to use. If problems are encountered, they will be documented in a bound field notebook. The faulty instrumentation/equipment will be scheduled for repair and sequestered and tagged until repaired and qualified for re-use.

3.5.2 Laboratory Instrument/Equipment

Laboratory instrument/equipment testing, inspection, and maintenance will be conducted in accordance with the procedures specified in the analytical laboratory QA manuals. The QA manual discusses the schedule, procedures, criteria, and documentation in place at the laboratory to prevent instrument and equipment failure and to minimize downtime. For each instrument or piece of equipment the laboratory maintains the following:

- Instrument/equipment inventory list;
- Instrument/equipment major spare parts list or inventory;
- External vendor service agreements (if applicable); and
- Instrument-specific preventive maintenance logbook or file.

The laboratory documents all preventive maintenance and repair for each instrument or piece of equipment in dedicated logbooks or files.

3.6 Instrument Calibration and Frequency

Calibration and frequency of calibration of both field and laboratory equipment are described in the following sections.

3.6.1 Field Instruments

The field equipment that will need calibration are listed below:

- GPS receiver
- Balance

Proper maintenance, calibration, and operation of each instrument will be the responsibility of field personnel assigned to a particular field activity. All instruments and equipment used during the field investigations will be maintained, calibrated, and operated according to the manufacturer's guidelines and recommendations.

3.6.2 Laboratory Equipment and Instrumentation

All laboratory equipment and instruments used for quantitative measurements are calibrated in accordance with the laboratory's formal calibration program as described in the QA manual. A summary of the laboratory instrument/equipment calibration program is presented. Detailed calibration procedures specific to each analysis are included in method-specific SOPs which can be obtained from the laboratory.

Whenever possible, the laboratory uses recognized procedures for calibration such as those published by USEPA or ASTM. If established procedures are not available, the laboratory develops a calibration procedure based on the type of equipment, stability, characteristics of the equipment, required accuracy, and the effect of operation error on the quantities measured. Equipment requiring only periodic calibration such as balances, thermometers, and micropipettors are listed along with their respective calibration requirements in the QA manual. Whenever possible, physical reference standards associated with periodic calibrations such as weights or certified thermometers with known relationships to nationally recognized standards are used. Where national reference standards are not available, the basis for the reference standard is documented.

Other instruments that require initial and/or continuing calibration as a part of instrument usage are listed along with their respective calibration requirements in the QA manual. Initial calibrations are verified and documented for each constituent by analysis of laboratory-prepared certified independent standard solutions. Chemical reference standards used in operational calibration are obtained from recognized standards suppliers and whenever possible are traceable to NIST, A2LA, or other recognized standards.

Equipment or instruments that fail calibration or become inoperable during use are tagged to indicate they are out of calibration. Such instruments or equipment are repaired and successfully recalibrated prior to re-use.

3.7 Acceptance Requirements for Supplies and Consumables

Supplies and consumables that may be used during field investigations include sample bottles, hoses, materials for decontamination activities, potable water, deionized water, and ASTM Type II water. Project team members obtaining supplies and consumables are responsible for assuring that the materials obtained meet the required specifications, are intact and in good condition, are available in adequate supply, and are stored appropriately until use. Project team members will direct any questions or identification of any problems regarding supplies and consumables to the Field Team Leader for resolution.

3.8 Data Acquisition Requirements (Non-direct Measurements)

This section of the QAPP describes the various sources and purpose of non-directly measured data that will be required for this investigation. The evaluation of the current site conditions requires a review of historical investigation reports that were prepared specifically for the Site.

3.9 Data Management

The objective of Data Management is to establish procedures to be used during the field investigations for documenting, tracking, and presenting investigative data. Data generated during the field investigations, as well as historical data, will be used to form the basis for conclusions and recommendations. Efficient utilization and comprehensive consideration of available data requires that the data be properly organized for review. Organization of the data shall be planned prior to actual collection to assure the generation of identifiable and usable data. This section contains procedures necessary to assure the collection of sufficient data for accurate validation of raw data and transfer of validated data to a data management system with which it can be evaluated with minimal effort. This section also describes the operating practices to be followed by personnel during the collecting and reporting of data.

3.9.1 Purpose and Background

Data collected during the field investigations will include analytical chemistry data from wild game samples, and data on physical conditions present at the site during sample collection. These data will be integrated into an analysis of the nature and extent of COPC in edible wild game tissue.

To complete this analysis, various computer programs will be utilized. The programs that are anticipated to be used are Microsoft Excel, Microsoft Access, Autodesk AutoCAD, SYSTAT, and Geographic Information Systems (GIS).

3.9.2 Data Recording

Observations made and measurements taken in the field will be recorded on appropriate project data sheets or in field logbooks. Upon completion of the field investigation, the data will be entered into a Database Management System (DBMS) and tabulated for evaluation and presentation in the field investigation report. Copies of the original data records will be attached to the report as appendices. Tissue matrix sample data will be summarized in tabular form in reports and will include sample location and other pertinent data.

All data used for meeting project objectives will be stored in an electronic database. This database will facilitate the following processes:

- Tracking COC and sample identification data;
- Reviewing and evaluating analytical data against project-specific QAPP criteria;
- Production of data tables.

The EDD will be submitted with the hard copy data reports. It is expected that the laboratories will perform a comparison of electronic data with the hard copy report prior to submittal to ensure that the EDD and hard copy data are identical. EDDs will be checked against the hard copy with 100% QA/QC for all detect analytes. The EDD should be submitted on a diskette (zip disk or CD-ROM), with the disk label including the Laboratory Delivery Group, submittal date, laboratory name, and site description. If the EDD is resubmitted, the EDD will be labeled as “Revised”.

3.9.3 Data Validation

Data validation is an integral part of the QA program and consists of reviewing and assessing the quality of data. Data validation provides assurance that the data are of acceptable quality as reported. For validity, the characteristics of importance are precision, accuracy, representativeness, comparability, and completeness. Data usability is the determination of whether or not a data set is sufficiently complete and of sufficient quality to support a decision or action, in terms of the specific DQOs. An outside firm or company specializing in data validation will independently validate analytical data generated during the project.

Analytical data will be generated by ENTRIX in EDD form, and will be submitted directly to the data validation firm for verification and validation. If necessary, exception reports will be produced. Qualified results will be loaded into the database and sent directly to ENTRIX.

The data validation process includes:

- Evaluating against laboratory and field blank criteria;
- Evaluating against accuracy criteria such as holding times, surrogates, laboratory control samples, and matrix spikes;
- Evaluating against precision criteria such as matrix spikes/matrix spike duplicates, and field and laboratory duplicates;
- Confirming that data qualifiers are assigned appropriately; and
- Uploading field sample analytical data only to the central database.

3.9.4 Data Transformation

If data transformation is performed for this study, then conversion procedures will be described in detail in the associated technical report.

3.9.5 Data Transmittal

Entering the data from field forms into the DBMS completes the integration of field data by data entry personnel. A staff scientist will review the data for completeness and accuracy by comparing the values to the original field data.

Analytical laboratory data are provided in both a hard copy and in EDD format. The electronic data are provided in a specified format that will be uploaded to intermediate files, reviewed for completeness and accuracy by the Project Liaison before uploading to the project DBMS.

3.9.6 Data Analysis

Data analysis (e.g. computation of summary statistics, standard errors, confidence intervals, etc.) will be conducted for this project.

3.9.7 Data Tracking

The Project Manager is ultimately responsible for all activities conducted during site activities, including data management. The Project Manager has the authority to enforce proper procedures as outlined in this plan and to implement corrective procedures to assure the accurate and timely flow and transfer of data. The Project Manager will review the final data reports.

Data will be generated from the field surveys and environmental sampling and analysis. The generators of data will be responsible for accurate and complete documentation of data required under the task, and for assuring that these data are presented to their supervisor in a timely manner.

The FTL will be responsible for the day-to-day monitoring of data collected in the field. He/she assures that data are collected in the format specified in this QAPP and route data to ENTRIX to be placed in the project files at the end of field collection activities. Original documents will be maintained in the ENTRIX central project file.

The FTL shall also be responsible for evaluating biological and field collected data. He/she reviews biological data for accuracy and completeness. The project manager for each component of the study will assure that representations of current site conditions are accurate and complete.

The Project Liaison will be responsible for the day-to-day monitoring of activities related to the generation and reporting of chemical data. He/she ensures that samples are analyzed according to the specified procedures; that data are validated; and that the data are properly coded, checked for accuracy (QA), and entered into the data management system. He/she assures the data are then routed to ENTRIX to be placed in the project files.

3.9.8 Data Storage and Retrieval

A project file will be established for the storage of original data, historical data, written documents, and data collected or generated during the field investigation. The format for the file will follow the central filing system procedure list, which consists of the following categories:

- Correspondence;
- Budgets;
- Contracts;
- Field Data
    - general field data
    - field notes
    - raw data
- Figures and Maps;
- Permits;
- Laboratory Data and QA/QC Documents;
- Chains of Custody;
- Photographs;
- Reports;
- Schedules;
- Background.

All materials will be dated, carry the initials of the person responsible for the preparation of the document, and bear the project number. The file copies will include peer review sign-off on the calculation sheets and editing review sheets where applicable.

Access to the project files will be limited to those personnel assigned to this project. The ENTRIX Project Manager maintains overall responsibility for the project files and assures that appropriate documents are filed. All documents relating to the project shall be controlled to assure proper distribution, filing, and retrieval. The document control shall also assure that revisions are properly recorded, distributed, and filed. ENTRIX staff maintain the project files.

ENTRIX staff will handle all documents submitted to the project file and will assure that the documents are appropriately filed by category and placed in the correct project file. Once filed, documents are available to ENTRIX staff and may be removed from file for use by signing out the material.

4.0 ASSESSMENT AND OVERSIGHT

This section presents the internal and external checks (assessments) that have been built into this project to assure that:

- Elements of this QAPP have been correctly implemented as prescribed for all investigations conducted;
- The quality of the data generated is adequate and satisfies the DQOs that have been identified in this QAPP; and
- Corrective actions, when needed, are implemented in a timely manner and their effectiveness is confirmed.

Assessment activities may include surveillance, inspection, peer review, management systems review, readiness review, technical systems audit, performance evaluation, and data quality assessment.

4.1 Assessment Activities

The following subsections identify the planned assessment and oversight activities to assure the objectives identified above are attained for field and laboratory operations. The QA Manager and/or the Project Manager may also identify additional assessment activities to be performed during the course of the project based upon findings of the planned assessment activities described below.

4.1.1 Assessment of Field Operations

The QA Manager and/or other designated members of the project team will conduct internal assessments of field operations, where appropriate. The assessment activities will evaluate field operations performance issues such as:

- Are sampling operations being conducted in accordance with the QAPP?;
- Are the sample labels being filled out completely and accurately?;
- Are the COC records complete and accurate?;
- Are the field notebooks being filled out completely and accurately?; and
- Are the sampling activities being conducted in accordance with SOPs?

Planned assessment activities to evaluate these and other field operations performance issues include surveillance (frequent review) of sample collection documentation, sample handling records (COC forms), field notebooks, and field measurements, and the performance of unannounced field operations audits.

The team member conducting the assessment activity will report the results of any assessment activities to the Project Manager. Assessment activity reports will include the findings and identification of any corrective actions taken or planned.

4.1.2 Assessment of Laboratory Operations

AgriQuality and Alta have performed congener-specific PCDD/F and PCB analysis for various clients and agencies in a variety of environmental matrices. The data generated for those projects have been approved. CRMs are analyzed routinely and the measured values are within ±20% of the actual concentrations. The laboratories also have ongoing internal audit programs implemented to monitor the degree of adherence to their policies, procedures, and standards. The internal audit program is described in the QA manual and includes systems audits, performance evaluations, data audits, and spot assessments. Laboratory personnel who are independent of the area(s) being evaluated will conduct internal audits. The laboratory also participates in external audits conducted by regulatory agencies and other clients. Project-specific assessments of laboratory operations are described below.

The Project Liaison will be in contact with the Project Manager on a weekly basis while samples collected during this investigation are being analyzed. This will allow assessment of progress in meeting DQO and the identification of any problems requiring corrective actions early in the investigative process. The Project Liaison will promptly report problems identified, corrective actions taken, and recommendations as appropriate for additional corrective action to the Project Manager. The Project Manager will review the problem and provide for the swift implementation of any outstanding corrective actions. In addition, contact between the Project QA Manager and the Independent Data Auditor (see Sections 5.1 and 5.3) could result in the need for a laboratory audit. The Project QA Manager will report the audit findings and any recommendations for corrective action to the Project Manager, the Project Liaison, and the laboratory. The Project Liaison will be responsible for working directly with the laboratory to assure the prompt resolution of any problems identified.

4.2 Reports to Management

This subsection discusses reports internal to the project team. External reports are discussed in Section 2.7.2.

Reports to management include project status reports, the results of surveillance evaluations, field and/or laboratory audits, and data quality assessments. These reports will be directed to the Project Manager who has ultimate responsibility for assuring that any corrective action response is completed, verified, and documented.

Final reports produced during this investigation will include a quality assurance section with the following information:

- Identification of problems that required corrective action and resolution of the problems;
- Data quality assessment in terms of precision and accuracy and how they affect the usability of the analytical results;
- Limitations of any qualified results and a discussion of any rejected results; and
- Discussion of the field and laboratory QA/QC sample results.

All written communications between project team members including reports to project management will be maintained in the project files.

5.0 DATA VALIDATION AND USABILITY

This section of the QAPP provides a description of the QA activities that will occur after the data collection phase of the project is completed. Implementation of this section will determine whether or not the data conform to the specified criteria, thus satisfying the project objectives.

5.1 Data Review, Validation, and Verification

Data validation is the process of reviewing data and accepting, qualifying, or rejecting data on the basis of sound criteria using established EPA guidelines. The laboratory will report laboratory data generated during field investigations as Level IV data packages. All of these data will be subjected to full data validation conducted by an independent data validator as discussed below in Section 5.1.1.

5.1.1 Independent Data Validation Protocols

While the actual procedures used will be determined by the validator the validation approach will consist of a systematic review of the analytical results, associated QC methods and results, and all of the supporting data. Specific data package review procedures can be found in SOP #802 “Data Package Review” included in this Work Plan. Best professional judgment in any area not specifically addressed by EPA guidelines will be utilized as necessary and described in the Usability Assessment portion of the data validation report.

Data will be validated according to applicable guidelines set forth in the following sources and guidelines to ensure compliance with the Federal Information Quality Act:

- “Data Package Review” SOP #802 Aquatic Toxicology Laboratory, National Food Safety and Toxicology Center, Michigan State University, E. Lansing, MI 48824-1222 USA
- “Guidance for Data Usability in Risk Assessment (Part A),” U.S. EPA Publication 9285.7-09A, U.S. EPA, April, 1992.
- “Guidelines for ensuring and maximizing the quality, objectivity, utility, and integrity of information disseminated by the Environmental Protection Agency” U.S. EPA Publication EPA/260R-02-008, October, 2002.
- “Guidelines for ensuring and maximizing the quality, objectivity, utility, and integrity of information disseminated by Federal Agencies.” Federal Register, 67, No. 36, pp8451-8460, February 22, 2002.

Data validations will include a data completeness check of each data package, a transcription check for sample results, and a thorough review of all laboratory reporting forms and the associated raw data for QA/QC issues. Specifically, this review will include:

- Review of data package completeness;
- Review of the required reporting summary forms and all associated raw data to determine if the QC requirements were met and to determine the effect of exceeded QC requirements on the precision, accuracy, and sensitivity of the data;
- Review of the overall data package to determine if contractual requirements were met (based upon National Functional Guidelines);

- Review of raw data and all calculations associated between one and a minimum of 10% of all samples to determine if the sample results and quantitation limits were correctly calculated and reported;
- Review of additional QA/QC parameters, such as field blank contamination, to determine technical usability of the data; and
- Application of standard data quality qualifiers to the data.

In addition, each data validation will include a comprehensive review of the following QA/QC parameters as indicated in the National Functional Guidelines:

- Holding times (to assess potential for degradation that will affect accuracy)
- GC/MS instrument check (to assess accuracy and sensitivity of method)
- Initial calibration (to assess method sensitivity)
- Continuing calibration (to assess method sensitivity)
- Blanks (to assess contamination for all compounds)
- System monitoring compounds (to assess method accuracy)
- MS/MSD or laboratory fortified blanks (to assess accuracy of the methods and precision of the method relative to the specific sample matrix)
- Internal standards (to assess method accuracy and sensitivity)
- Target compound identification
- Compound RL and MDL (to assess sensitivity as compared to project-specific requirements)
- System performance (to assess accuracy and precision)

5.1.2 ENTRIX Internal Data Quality Control Procedures

ENTRIX has established an internal QA Program to assure that all project analytical data are tracked within a COC database system and are of reliable and comparable data quality. The Project QA Manager will be responsible for assuring that ENTRIX internal QC procedures are followed for all project analytical data.

The COC database system allows ENTRIX to track samples and their analytical results to ensure that the project data quality objective for completeness is met. Samples and analytical data are tracked in a COC database system by their COC number. The COC number along with the date the laboratory received the samples for analyses are entered into the COC database system from the information on the field copy of the COC. When the final laboratory reports are completed, the laboratory report number along with the date and initials of the ENTRIX personnel who have reviewed the report is entered into the COC database system according to the COC number.

A limited internal data validation is performed on all project analytical data when the final report is reviewed by ENTRIX. The limited data validation will include a data completeness review of each data package, and a limited review of QA/QC parameters as indicated in the National Functional Guidelines to assure that all project analytical data are of reliable and comparable data quality. Specifically, the following QA/QC parameters will be reviewed:

- Holding times (to assess potential for degradation that will affect accuracy);
- Blanks (to assess contamination for all compounds);
- MS/MSD or Laboratory Control Spike/Spike Duplicates (to assess accuracy of the methods and precision of the method relative to the specific sample matrix);
- Internal Standards (to assess method accuracy and sensitivity);
- Compound RL and MDL (to assess sensitivity as compared to project-specific requirements); and
- Field Duplicate RPDs (to assess precision of the method relative to field sampling techniques, the specific sample matrix, and representativeness of the sample aliquot to the area sampled).

The results of this limited data validation and any corrective actions implemented are recorded on a QA/QC worksheet. The data reviewer will initial and date the QA/QC worksheet. The Project Manager will provide secondary review of the QA/QC worksheet and will also initial and date the QA/QC worksheet. The initialed and dated QA/QC worksheet will be attached to the final analytical laboratory report that is retained in the project files.

5.2 Validation and Verification Methods

The data validation process is conducted to assess the effect of the overall sampling and analysis process on the usability of the data. There are two areas of review: laboratory performance evaluation and the effect of matrix interferences. Evaluation of laboratory performance is a check for compliance with the method requirements and is a straightforward examination. The laboratory either did or did not analyze the samples within the QC limits of the analytical method and according to protocol requirements. The assessment of potential matrix effects consists of a QC evaluation of the analytical results and also the results of testing blank, duplicate, and matrix spike samples, and then assessing how, if at all, the matrix effect will impact the usability of the data.

All analytical data will be supported by a data package. The data package contains the supporting QC data for the associated field samples. The data validation report deliverables will include the following information:

- A comprehensive narrative detailing all QC exceedances, explaining qualifications of data results. In cases where data are qualified due to quantifiable QC exceedances, the bias (high or low) will be identified;
- Data summary tables in Microsoft Access format reporting all data results with the qualifiers that were added during the data validation review. These tables will include sample ID, laboratory ID, date sampled, sample type (e.g., field duplicate, field blank), units, concentration of analytes, and validation qualifiers. These tables may be modified to report other information as needed (such as depth of soil samples, date analyzed, dilution factor);
- Re-submittal requests sent to the laboratory indicating missing information, verification of analytical information, etc.; and
- EDDs will be compatible with the project database. These electronic deliverables will contain the validated results and qualifications as presented in the data summary tables of the validation reports. Additionally, the validation reports can be submitted in electronic format for inclusion in interim RI data deliverables.

Before the laboratory releases each data package, the laboratory must carefully review the sample and laboratory performance QC data to verify sample identity and also the completeness and accuracy of the sample and QC data. This is performed through three levels of laboratory data review starting with 100% verification performed by the laboratory analyst, followed by a second-level review performed by a peer, supervisor, or designee. The laboratory Project Manager performs the third and final laboratory review to assure that project requirements are met for the analyses performed.

Data validation is at times based on best professional judgment. In order to achieve consistent data validation, data worksheets will be completed for each data validation effort. A data review worksheet is a summary form on which the data validator records data validation notes and conclusions specific to each analytical method. The worksheets will help the validator to track and summarize the overall quality of the data. Sample results will then be qualified as appropriate, following EPA protocols. Samples that do not meet the acceptance limit criteria will be indicated with a qualifying flag, which is a one or two-letter abbreviation that indicates a problem with the data (Table 5-1).

The data verification process begins once the data packages for each project have been validated. During verification, the entire data set will be verified for overall trends in data quality and usability. Information summarized as part of the data quality verification will include frequencies of detection, dilution factors that might affect data usability, and patterns of target compound distribution. The data set also will be evaluated to identify potential data limitations or uncertainties in the laboratory. The trend analysis results will be included in the validation summary report, which will be submitted to the Project Manager at the end of the field effort. The validation report and notes will be archived with the analytical data.

5.3 Reconciliation with User Requirements

The Independent Data Auditor will provide an assessment of the usability of the validated data compared to the data validation criteria and DQOs. The usability assessment will be performed based on Guidance for Data Usability in Risk Assessment (EPA 1992) and best professional judgment. The Independent Data Auditor will delineate major and minor deficiencies in the data, their effects on the reported results, and determination of usability for each compound reported in each sample included in the data package. The usability assessment will provide an overall summary of data quality. It defines acceptability or problems with accuracy, precision, sensitivity, and representativeness of the results with clear guidance to the data users of the uncertainties in the data that have been qualified as estimated (J) and a quantification of these uncertainties (e.g., bias high by a maximum of 80%), wherever possible. The Independent Data Auditor may determine specific results to be unusable because of cumulative effects of QC exceedances. Alternatively, based upon the EPA guidelines and best professional judgment, the Independent Data Auditor may determine specific results to be usable for DQOs when they are not significantly outside the QC criteria.

The final activity of the data validation process is to assess whether the data meets the DQOs. The final results, as adjusted for the findings of any data validation/data evaluation, will be checked against the DQOs and an assessment will be made as to whether the data are of sufficient quality to support the DQOs. The decision as to data sufficiency may be affected by the overall precision, accuracy, and completeness of the data as demonstrated by the data validation process. If the data are sufficient to achieve project objectives, the project manager will release the data and work can proceed. If the data are insufficient, corrective action will be required.

Table 5-1. Data Validation Qualifiers.

Qualifier	Explanation of Qualifier
Organic Analyses	
U	The compound was analyzed for, but was not detected above the reported method detection limit.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
R	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.
UJ	The analyte was not detected above the reported method detection limit. However, the reported limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
Inorganic Analyses	
U	The compound was analyzed for, but was not detected above the reported method detection limit.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
R	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.
UJ	The analyte was not detected above the reported method detection limit. However, the reported limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
B	The analyte was positively identified; the reported concentration is greater than the instrument detection limit, but less than the QAPP specified Reporting Limit.

6.0 REFERENCES

6.1 General

ASTM D 2216-90. Moisture Analysis of Soils.

ASTM D 422-63. Standard Test Method for Particle-Size Analysis of Soils.

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U.S EPA (United States Environmental Protection Agency). 2002. Guidelines for ensuring and maximizing the quality, objectivity, utility, and integrity of information disseminated by the Environmental Protection Agency" U.S. EPA Publication EPA/260R-02-008, October, 2002.

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6.2 Associated Standard Operating Procedures

SOP #	Title
203	Homogenization of Tissue Samples
213	PCDD/F Congeners in Sediment and Tissue samples.
212	Glassware Cleaning: General and Trace Organic Analysis
229	Protocol for Sampling and Analysis of Cottontail Rabbits (*Sylvilagus floridanus*)
230	Protocol for Sampling and Analysis of Wild Turkey (*Meleagris gallopavo*)
231	Protocol for Field Sampling White -Tailed Deer (*Odocoileus virginianus*)
401	Sample Management: Receiving, Preservation, Storage, Documentation, Decontamination, and Disposal
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802	Data Package Review

Appendix C. Site Specific Health and Safety Plan (S-HASP)

DRAFT

DRAFT SITE-SPECIFIC HEALTH AND SAFETY PLAN FOR FIELD SAMPLING ACTIVITIES IN SUPPORT OF THE WORK PLAN FOR THE INTERIM RESPONSE ACTIVITY OF EVALUATING WILD GAME TAKEN FROM THE TITTABAWASSEE RIVER FLOODPLAIN

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1.0 INTRODUCTION

This Site-Specific Health and Safety Plan (S-HASP) delineates the basic safety requirements for field sampling activities to be performed on the Tittabawassee River site (referred to hereafter as the Site) in support of the wild game workplan. The Tittabawassee River site as defined in the Hazardous Waste Management Facility Operating License (issued on June 12, 2003 by Michigan Department of Environmental Quality to The Dow Chemical Company) includes approximately 23 miles of the Tittabawassee River from the upstream boundary of The Dow Chemical Company to the confluence of the Tittabawassee and Shiawassee Rivers downstream of Greenpoint Island. Planned activities include the collection of rabbits and/or squirrels, turkeys, and white-tailed deer. Fieldwork for the wild game workplan is expected to occur throught mid to late Fall, 2003.

This S-HASP is prepared in compliance with the requirements of the Federal OSHA Hazardous Waste Operation and Emergency Response Standard (HAZWOPER; 29 CFR 1910.120).

The provisions set forth in this S-HASP apply to the personnel of ENTRIX, Inc. and related subcontractors engaged in field activities in support of the wild game workplan. Subcontractors may elect to modify these provisions, but only to upgrade or increase safety activities. It is noted that this S-HASP may not thoroughly address all hazards associated with any specialized subcontractor operations. In this situation, subcontractors shall be responsible for developing their own health and safety procedures to adequately address their scope of operations at this site. ENTRIX, Inc. may retain subcontractors to hunt both white-tailed deer and turkey.

This S-HASP addresses the expected potential hazards that may be encountered for this project. If unanticipated changes in site or working conditions occur which are not addressed by this plan, addenda will be provided by ENTRIX, Inc.

1.1 Site Location and Background

The Tittabawassee River is located in central Michigan, and begins at the confluence of the Tobacco and Molasses Rivers. As part of the Saginaw River watershed, the Tittabawassee flows from the north through Midland in a southeastern direction to the confluence with the Saginaw River and eventually to Saginaw Bay. The distance between Midland and the confluence with the Saginaw River is approximately 23 river miles.

1.2 Scope of Work

The overall objective of the proposed study is to gain a better understanding of the concentrations of PCDD/Fs that may be available to humans via consumption of wild game animals from the Tittabawassee River floodplain.

The following animals will be the focus of the wild game workplan:

- Rabbits and/or squirrels
- Wild turkey
- White-tailed deer

2.0 PROJECT SAFETY AUTHORITY

ENTRIX, Inc. personnel responsible for project safety are the Project Manager and the Site Health and Safety Officer (HSO) or his/her designee. In addition, Field Team Leaders will be responsible for project safety for their specific tasks. The Project Manager is responsible for the provisions and submittal of this plan, and for advising the HSO on health and safety matters. The Project Manager has the authority to provide for the auditing of compliance with the provisions of this plan, suspension or modification of work practices, and administration of disciplinary actions for individuals whose conduct does not meet the requirements set forth herein. The Project Manager may elect to give the HSO authority to administer disciplinary actions for individuals whose conduct does not meet the requirements set forth herein.

The HSO is responsible for the dissemination of the information contained in this plan to all personnel assigned to the project, and to the responsible representative of each subcontractor firm working under ENTRIX, Inc. on the project. The Field Team Leaders (FTL) will be responsible for task-specific health & safety. As such, he or she is responsible for performing or providing the following as necessary:

- Adequate on-site safety supplies & equipment inventory (see list of protective equipment, Sec. 7.0).
- Verification of 40-hour HAZWOPER and applicable HAZWOPER updates, supervisor training, and/or medical monitoring and fit test certifications for all potentially exposed on-site personnel.
- Tailgate discussion of site safety plan. Documentation of tailgate safety meetings in field notebook.
- Documentation of all accidents or safety plan violations per the incident reporting and investigation procedures provided in Appendix F of this S-HASP.
- Emergency contacts as needed.

The HSO or FTL has the authority to suspend work any time he or she determines that the health and safety practices at the site are inadequate and shall also inform the Project Manager of individuals whose conduct is not consistent with the requirements of the plan. The HSO or FTL has the responsibility to check in with any identified safety contact each day before commencing field operations. The HSO or FTL will disseminate any new information provided to the field team during tailgate safety meetings.

3.0 SAFETY/ORIENTATION TRAINING

This section presents the general and site-specific training requirements for this project in accordance with regulatory, client, and/or ENTRIX, Inc. requirements. Personnel will provide proof of required training to the HSO for inspection prior to performance of any subject field activities. The HSO will be responsible for reviewing the proof of required training in accordance with the requirements described below and documenting this review in the field notes before job start up.

3.1 General Training Requirements

General training requirements that apply to personnel on this project are described below.

3.1.1 First Aid

At least one team member on every field team shall have current first aid training including adult CPR training. Current training for the purposes of this S-HASP is as follows: 1) First Aid training current within 3 years and 2) Adult CPR current within 1 year.

3.1.2 Medical Monitoring

It is not anticipated that medical monitoring will be necessary for activities performed on this project.

3.1.3 Respirator Training and Fit Testing

It is not anticipated that any respirator training or fit-testing will be required for any activities performed on this project. However, if respirators are required, then team members shall have respirator training on APRs and fit-testing current within one year. Fit-testing shall be performed on the make, model and size of the full-face APR to be worn for any required task.

3.2 Site-specific Training

Field personnel including volunteers and subcontractors will review this S-HASP before beginning work as part of the site-specific safety training for this project. The HSO or FTL will conduct a tailgate safety meeting to review the S-HASP before the start of field operations that may substantiate prior review of the S-HASP or serve as the primary review. Field personnel will certify their review by signing a S-HASP training record form (Appendix B) or signing the field notebook after the tailgate safety meeting. The Project Manager or HSO is responsible for distributing this S-HASP to appropriate personnel and verifying review by obtaining signed review forms or copies of field notes. Signed review forms or copies of field notes with signatures will be placed in project files.

Whenever a change of conditions on-site occurs that may affect safety, the HSO or FTL will conduct a tailgate safety meeting if appropriate. Changing site conditions that may affect safety include the following:

- Change of field personnel (volunteer or subcontractor);
- Change in work activity;

- Change in weather conditions; and
- Visitors on site.

All training sessions, safety meetings, and safety briefings will be documented by the HSO or FTL in the field notebook or on Tailgate Safety Meeting Record forms (Appendix C). Documentation will include a brief description of topics addressed and the signatures of all training attendees.

4.0 HAZARD ASSESSMENT

This section presents the identification of general, task or activity-specific and site-specific hazards and control measures associated with planned field activities for this project. The general hazards and protective measures expected during the Site field activities and methods used to promote worker safety are presented in Table 5-1. Physical, chemical, and biological hazards and control measures are addressed separately and more completely in the following sections.

4.1 Physical Hazards

General physical hazards that may be present during field sampling activities include the following:

- Misfire of rifles or shotguns causing injuries;
- Falls from elevations such as trees perches;
- Tripping over tools, equipment or uneven terrain;
- Slipping on wet or oily surfaces;
- Manual lifting;
- Exposure to noise generated by firearms;
- Insufficient or faulty protective equipment;
- Insufficient or faulty operations, equipment, or tools; and
- Storm events accompanied by high winds and/or lightning.

4.1.1 Site-Specific Hazards

The sampling sites on this project may require climbing over relatively steep, uneven, or heavily vegetated terrain. Other site-specific hazards include:

- Trip, slip, and fall hazards from walking and/or kneeling on potentially uneven, steep, and/or slippery terrain.
- Cold stress from low environmental air temperatures
- Sunburn, windburn;
- Damage to eyes from sun exposure (UV radiation); and
- Manual lifting of deer and/or turkey carcasses.

Safety precautions for general and site-specific hazards are addressed in Section 7.0.

4.2 Chemical Hazards

During the conduct of wild game sampling and processing, various chemicals may be used for decontamination purposes. Two solvents that will be used in the decontamination process are acetone and hexane. Material Safety Data Sheets (MSDS) for acetone and hexane are provided in Appendix D. While concentrations of PCDD/F in wild game animals are the subject of this investigation, these chemicals do not pose an immediate hazard to field personnel since they are tightly bound to soils and sediments.

4.3 Biological Hazards

Multiple biological hazards may be present in the Site and are identified and discussed below. Protective measures for each biological hazard identified are also included in the following discussion. Field personnel shall carefully review this section.

4.3.1 Snakes

Snakes are common in the Site. Personnel should be extremely careful when walking through tall grass, rocks, or debris. If a snake is encountered, slowly and quietly back away from the snake. Inform all personnel at the site of its location. Do not attempt to move or kill a snake because certain species are protected under state and federal laws. In the event of snakebite, do not try to move the affected limb; wait for transportation. The venom should be wiped off the skin because it will attack intact skin.

4.3.2 Bovine tuberculosis

Bovine tuberculosis (TB) presents a potential hazard at the Site. Bovine TB is a disease caused by the bacterium *Mycobacterium bovis* (a different strain of mycobacterium than usually infects humans), and has been found in a few deer populations in Michigan. While it is possible to transmit bovine TB from animals to people, the likelihood is extremely rare. It is very unlikely that a person field-dressing deer infected with bovine TB would become infected. As a precaution, personnel handling deer in the field and laboratory shall wear disposable latex gloves and shall wash their hands following any handling of deer carcasses. The Michigan Department of Natural Resources (MDNR) will test all deer collected from the Site for bovine TB prior to necropsy.

4.3.3 Chronic wasting syndrome

Chronic wasting disease (CWD) is a transmissible neurologic disease of elk and deer characterized by loss of body condition, behavioral abnormalities, and always resulting in death to the animal. According to public health officials, there is no evidence that CWD can be naturally transmitted to humans, or to animals other than deer and elk. Although there is no evidence that chronic wasting disease affects humans, all personnel shall take reasonable precautions, such as wearing protective gloves when handling deer, minimizing handling of brain or spinal cord tissues during deer necropsy, and washing hands thoroughly following deer handling activities.

4.3.4 Insects

Bees, wasps, yellow jackets, black widow, and brown recluse spiders present a potential hazard at the site, especially for those individuals sensitive to those bites or stings. Before initial assignment on the project, personnel with known allergic responses to insect stings shall make their field supervisor aware of this condition. In all cases, a person suspected of being bitten by a black widow or brown recluse spider shall receive medical attention. The venom from the brown recluse spider is capable of causing coma and kidney failure in its victim. Protection against insects, such as protective clothing, repellents, extermination, and training in recognition and identification of harmful insects, may be employed.

4.3.5 Ticks

Ticks transmit many diverse etiologic agents. Diseases transmitted by the tick include Lyme disease, Rocky Mountain Spotted Fever, and other viral and rickettsial diseases. Ticks are normally found in wooded and bushy areas. When walking through tall brush areas, periodically check yourself and your coworkers for ticks. Ticks burrow into the skin. It is essential to remove the entire tick as soon as it is found.

4.3.6 Poisonous Plants

Poisonous plants may be present at the site, including poison ivy, poison oak, and poison sumac. The plants contain a resin that causes a delayed allergic hypersensitivity reaction on contact. The resin is active in live, dead, dry, and burned plant parts, and it may be carried through the air. Signs and symptoms are usually evident within 24 to 48 hours after exposure, including burning, stinging, and blisters. Notify the health and safety officer (or designee) if these plants are observed. If exposure or contact occurs, wash the affected area first with rubbing alcohol followed by soap and water, but do not spread the resin to uncontacted areas.

4.3.7 Vermin

Rats, mice, squirrels, and rabbits are carriers of disease. The most serious are rabies, plague, and Hantavirus. Fully 50 percent of Hantavirus victims die from the disease. Vermin bites should be reported immediately to the health and safety officer (or designee) and proper medical care shall be obtained.

4.4 Task-Specific Hazards

The following tasks have task-specific hazards and control measures as described below.

4.4.1 Firearms

Mishandling of firearms can result in serious injury or death. The use and possession of firearms on Site must be in accordance with all Federal, State, and local laws and regulations. Firearms shall not have a cartridge in the chamber while in a motor vehicle. Firearms left or stored in unattended vehicles must be placed out of public sight and the vehicle locked. Firearms will not be worn, carried, or used in an irresponsible, unsafe, or unprofessional manner. Firearms will not be used if they present a danger to life or property or if a problem with public relations may result. All personnel on the Site, required or requested to use firearms during the collection process will be provided safety and handling training. Examples of acceptable training would be informal field and/or classroom training conducted by appropriate personnel knowledgeable in firearms safety, self-instructed video training, formal classroom training from firearms professionals, or a combination of each.

4.5 Subcontractor-Furnished Equipment

Each subcontractor is responsible for the proper and safe operation of all equipment he brings to the site.

Table 4-1. Hazards and protective measures.

Potential Hazards	Methods to Ensure Worker Safety
Injuries caused by tripping or falling	Job site reconnaissance will be conducted to identify hazards.
Lifting, manual labor	The site HSO or designee will identify ergonomic factors and will develop measures to prevent injury. Proper lifting techniques and warm-up will be used before strenuous tasks. Special hand protection will be required where indicated.
Firearms	All personnel carrying firearms will be properly trained. Caution will be exercized in all aspects of firearm use. Local, State, and federal firearm laws will be followed throughout the collection process.
Bovine TB	Protective clothing, such as latex gloves will be worn during deer handling. MDNR will test deer for TB prior to necropsy and further handling. Additional PPE may be needed if TB is detected in deer from the Site.
Chronic wasting disease	Protective clothing, such as latex gloves will be worn during deer handling.
Poison plants	Site screening, protective clothing, removal of plants, or skin creams will be used.
Snakes	Site screening, protective clothing, training, and on-site first-aid kits will be used for remote work locations.
Solar radiation	Protective clothing or sunblock will be worn.
Weather	If lightning or thunder is seen or heard, then all personnel will cease sampling and retreat to a safe location until the threat of lightning passes.
Stinging insects such as wasps and bees	The HSO will identify areas where workers could contact stinging insects and will determine actions needed to rectify the problem. Workers will not be allowed to work near insects where an unreasonable risk is present.
Other Insects	Inspection for ticks and other biting insects should be performed when leaving the site, particularly wooded areas.
Wild animals	Site screening will be used. Hantavirus precautions may be required.

Note:

HSO	Site Health and Safety Officer
PPE	Personal Protective Equipment
MSDS	Material Safety Data Sheet

5.0 AIR MONITORING AND CONTROL MEASURES

Airborne exposure is generally not a concern with dioxin in soils. Dioxins are generally not volatile at ambient temperatures. In addition, dioxins absorb to soils tightly so the volatization rate of dioxins affixed to soils is quite low. Given the low volatility of dioxins, in all probability, airborne concentrations of dioxins would not be detectable at any level. Therefore, air monitoring is not required for any activities on this project.

6.0 GENERAL PROJECT SAFETY REQUIREMENTS

6.1 General Safety Precautions

The project operations shall be conducted with the following minimum safety requirements employed:

- No person shall ever be at a field site alone
- Responsible parties will be notified when any person goes into the field. Notification will include dates and locations.
- If present in the field during legal hunting periods, personnel will wear hunter orange (a hat, cap, vest, jacket or rain gear).
- Firearms will be handled safely, as if loaded. The muzzle of the gun should at all times be pointed in a safe direction, with the safety on until ready to shoot.
- A cellular phone or communication radio will be carried on all field outings. Always test to see if this equipment is operational be for departing for site and immediately upon arrival to site.
- Eating, drinking, chewing gum or tobacco, smoking, or any practice that increases the probability of hand-to-mouth transfer and ingestion of material shall be prohibited during sample collection.
- Eating and drinking will be restricted to areas outside the operations area.
- Closed toe and heel shoes or boots with good traction appropriate for walking on uneven surfaces will be worn.
- Hats, long-sleeve shirts, long pants and sunscreen will be worn as appropriate to prevent sunburn/windburn.
- Layers of clothing are recommended to prevent hypothermia or heat stress.
- All personnel shall be required to wash or wipe hands and face before eating or drinking.
- Legible and understandable precautionary labels shall be prominently affixed to containers of scrap, waste, debris, and contaminated clothing.
- All wastes generated from project activities (soiled PPE, etc.) shall be contained and disposed of in accordance with procedures for investigation-derived waste (see Section 8.0).
- The HSO and all field employees will be responsible to identify and alert other field team members to physical hazards present at the site.
- All employees will be provided access and be responsible to read the appropriate safety manuals.

Additional safety precautions for specific operations are described in Section 8.0.

6.2 Forbidden Practices

The following practices shall be strictly forbidden during any work on site:

- Horseplay
- Fighting
- Use of facial cosmetics other than prescription medication, sunscreen, or as prescribed on the advice of a physician.
- Climbing on or over obstacles
- Starting or maintaining an open flame of any type unless authorized by the HSO
- Entering the work site with safety equipment that has not been determined to be in working condition immediately before entry
- Entering the work site, under any circumstances, by an employee or visitor without prior approval

In addition to the forbidden practices, the HSO may impose other prohibitions that may be required for safe operations.

6.3 Cold Stress

During cold weather, about 60 percent of a person's body fuel is used to heat the body. When exposed to cold temperatures for extended periods of time, a person tires easily and exposed skin cools rapidly. Individuals working in these conditions are at risk for developing hypothermia and frostbite. When immersion in water is a possibility, workers in cold weather situations are also at risk for trench foot. This section provides information on cold-related injuries, risk factors, harmful effects of cold and first aid measures for injuries, and prevention of cold-related disorders.

6.3.1 Cold and the Body

A person gains heat from food and muscular activity and loses it though convection, conduction, radiation, sweating. These processes work together to maintain a constant body temperature. When body temperature drops even a few degrees below normal (98.6°F or 37°C), the blood vessels constrict, decreasing peripheral blood flow to reduce heat loss from the surface of the skin. Shivering generates heat by increasing the body's metabolic rate.

There are four environmental conditions that cause cold-related stress:

- Low temperatures;
- High/cool winds;
- Dampness; and
- Cold water.

Wind chill or equivalent chill temperature (ECT), a combination of air temperature and wind speed, is a crucial factor to evaluate when working outside because it directly effects the rate of heat loss on the human body. A table to determine the ECT based on ambient temperature and wind speed is provided in Appendix E.

6.3.2 Cold-Related Risk Factors

Sucsceptibility to hypothermia is increased by the following factors:

- Wearing inadequate or wet clothing.
- Taking certain drugs or medications such as alcohol, nicotine, caffeine, and medication that inhibits the body's response to cold or impairs judgement.
- Exhaustion, dehydration, injury or immobilization.
- Recent or current illness such as cold or flu, chronic health conditions such as diabetes, heart, vascular, and thyroid problems.

6.3.3 Harmful Effects of Cold

The harmful effects of over-exposure to cold are discussed below including symptoms and first aid measures.

6.3.3.1 General Hypothermia

Hypothermia occurs when body temperature falls to a level where normal muscular and cerebral functions are impaired. While associated with freezing temperatures, hypothermia may occur at temperatures well above freezing. Hypothermia is a potentially life-threatening condition. Pain in the extremities may be the first early warning sign of danger from cold stress. Violent shivering is also an early sign of hypothermia. During cold exposure, maximum severe shivering occurs when the body temperature has fallen to 95°F (36°C). Other symptoms of hypothermia include strange or irritable behavior, slurred speech and/or clumsiness. As hypothermia progresses, vision becomes impaired, and the victim may stagger and fall, followed by numbness or sleepiness. Unconsciousness and full heart failure can occur with severe hypothermia. The onset of pain in the extremities, heavy shivering, feeling of excessive fatigue, drowsiness, irritability or euphoria are indications to immediately return to a heated warm shelter.

Treatment of hypothermia involves conserving the victim's remaining body heat and providing additional heat sources. Reduction of heat loss can be accomplished by the following: obtaining shelter, removing wet clothing, adding layers of dry clothing, blankets and/or using a pre-warmed sleeping bag. External rewarming techniques include body-to-body contact (e.g., placing the person in a prewarmed sleeping bag with a person of normal temperature), chemical heat packs, or insulated hot water bottles. Good areas to place warming packs are the armpits, neck, chest and groin.

Handle hypothermic people gently because of the increased irritability of the cold heart. Seek medical assistance for persons suspected of being moderately or severely hypothermic. If a person is not responding and not shivering, assume he or she is severely hypothermic.

6.3.3.2 Frostbite

Frostbite occurs when skin tissue actually freezes, causing ice crystals to form between cells and draw water from them, which lead to cellular dehydration. Although, this usually occurs at temperatures below 30°F (-1°C), wind chill effects can cause frostbite at above-freezing temperatures.

Initial symptoms of frostbite include uncomfortable cold and tingling sensations, stinging or aching feeling of the exposed area followed by numbness. Ears, fingers, toes, cheeks, and noses are primarily affected. Frostbitten areas appear white and cold to the touch. The appearance of frostbite varies depending on whether rewarming has occurred. Deeper frostbite involves freezing of deeper tissues such as muscles and tendons, causing exposed areas to become numb, painless and hard to the touch.

If frostbite is suspected, seek immediate medical assistance. Frostbitten parts should be covered with dry sterile gauze or soft, clean cloth bandages. Do not massage frostbitten tissues because this may cause greater injury. Take measures to prevent further cold injury.

6.3.3.3 Trench foot

Trench foot is caused by long, continuous exposure to a wet, cold environment, or actual immersion in water. Symptoms include a tingling and/or itching sensation, burning, pain, and swelling, sometimes forming blisters in more extreme cases. Move individuals to a warm, dry area where the affected tissue can be treated with careful washing and drying, rewarming and slight elevation. Seek medical assistance as soon as possible.

6.3.4 Preventing Cold-related disorders

Workers should be protected from exposure to cold so that deep core temperature does not fall below 96.8°F (36°C); lower body temperatures will likely result in reduced mental alertness, reduction in rational decision making, or lack of consciousness. The following measures shall be implemented to prevent general hypothermia, frostbite and trench foot from occurring during outdoor field activities.

6.3.4.1 Personal Protective Clothing

Adequate insulating dry clothing must be worn if work is performed in ECT below 40°F (4°C). At least three layers of clothing are recommended including the following:

- An outer layer to break the wind and allow some ventilation.
- A middle layer of down or wool to absorb sweat and retain insulation when wet.
- Inner layers of cotton or synthetic weave to allow ventilation.

Pay special attention to protecting feet, hands, face and head. Up to 40% of body heat can be lost when the head is exposed. Footgear should be insulated to protect against cold and dampness. Keep a change of clothing available in case work garments become wet.

6.3.4.2 Safe Work Practices

The following additional guidelines shall be followed to prevent or minimize the risk of injury to cold stress:

- In cold field conditions, warm sweet drinks and soups are recommended to provide caloric intake and maintain fluid volume. Consumption of coffee and other caffeinated beverages should be limited because of the diuretic and circulatory system effects.

- Wet clothing at ECT of 35.6°F (2°C) or less shall be considered a life-threatening situation. Workers shall change into dry clothing immediately and return to a heated warm shelter for monitoring.
- To prevent injury to exposed skin (ears, head, cheeks, hands, etc.), continuous exposure shall be avoided when the ECT is –25.6°F (-32°C) or less.
- No solo fieldwork will be conducted at or below 10.4°F (-12°C) ECT.

7.0 PROTECTIVE EQUIPMENT REQUIREMENTS

7.1 Personal Protective Equipment

Personal protective equipment (PPE) consists of three components: standard safety equipment required on the site, special PPE (fall protection, water safety), and respiratory protective equipment. All personnel are expected to come to work with proper safety equipment as provided by ENTRIX, Inc. In addition, all project and subcontract personnel entering a site shall comply with any activity-specific safety requirements.

7.1.1 Equipment

The equipment level required for a given field activity will be determined by the HSO and the start of work in consultation with the ENTRIX, Inc. Health and Safety Officer (HSO). This level of equipment may be revised as site conditions change. A detailed description of the proposed initial PPE ensemble for tasks with identified chemical exposure is presented in Table 7-1. The level of equipment required at the site will depend on the activities being performed.

7.1.1.1 Basic Protective Clothing and Equipment

The minimum required PPE for the Site consists of the following:

- Fully enclosed hard-soled shoe or boots;
- Long pants;
- Long-sleeved shirts;;
- Hunter orange (cap, vest, etc.);
- Maps
- Cell phones and/or 2-way radios

Contractors will provide their own PPE.

Table 7-1 shows the PPE required for activities specific to areas and/or type of media sampled.

Table 7-1. Personal protective equipment (PPE).

Activity	Level	Body	Respirator	Skin	Other
Basic PPE					
All activities	D	Standard	None required	None required	Hunter orange

8.0 DECONTAMINATION/CONTAMINATION REDUCTION PROCEDURES

8.1 Decontamination

A decontamination station will be designated, configured, and secured at the site if appropriate. All contaminated personal protective equipment (PPE) will be transferred to designee for proper disposal. Personnel shall always wash hands and exposed skin after removing protective clothing or leaving level D controlled work areas (basic decontamination level). Selected sampling equipment as designated in the Sampling and Analysis Plan, Quality Assurance Project Plan, and standard operating procedures, will be decontaminated using hexane/acetone, followed by DI water to prevent cross-contamination between samples. Hexane rinse water and any solid waste generated will be disposed of at the appropriate laboratory facilities in accordance with local, state, and federal regulations.

8.2 Subcontractor Requirements

Each subcontractor shall decontaminate equipment as necessary to meet technical requirements. Subcontractors are responsible for decontamination of equipment to the satisfaction of the HSO or FTL.

9.0 EMERGENCY RESPONSE PROCEDURES

This section describes project-specific procedures to be followed in case of an emergency and emergency equipment to be taken into the field. Project personnel shall carefully review and adhere to the emergency response and notification procedures described in this section.

9.1 Emergency Communications

Each field team will have a reliable means of contact with offsite emergency services. Most often this means of contact will be a cellular telephone. In addition, if field team members will be working out of visual contact with each other, then a reliable means of communication with other field team members will be established. Depending on the situation this could be horns, whistles, hand-held two-way radios or cellular telephones. If horns or whistles are used as an emergency communication device, three blasts will be used as a distress signal. Field personnel working alone will be required to report into a designated contact at prescribed intervals not less than at the end of each field day so that a timely search and rescue effort can be initiated. When firearms are in use in the field, regular communication chek-in times will be established at the tailgate safety meetings prior to start of the field work.

9.2 Emergency Equipment

A first aid kit and bloodborne pathogen (BBP) kit will be taken into the field each day throughout the project. Additional kits will be provided for each field team if field teams will be working in separate locations to assure immediate access to first aid and BBP supplies.

9.3 General Emergency Procedures

In the event of a fire, explosion, physical injury or an illness due to chemical exposure, the appropriate parties should be contacted using the phone numbers listed at the end of this section. The HSO or FTL is responsible for evaluating the seriousness of the situation and making the appropriate notifications.

9.3.1 Blood-Borne Pathogen Exposure Control Plan

All personnel should be aware of the potential to transmit disease from contact with body fluids. Personnel should assume that all bodily fluids are potentially infectious and use appropriate precautions. Controls to be considered are as follows:

- Use of the victim's hand to control initial bleeding;
- Use of available protective gear (Tyvek®, gloves) to prevent contact;
- Wash promptly after contact with body fluids;
- Use rescue breather for CPR.

9.3.2 First Aid Supplies

First aid kits will be maintained during all field activities on site. The HSO or FTL shall periodically verify that first aid supplies are available. Trained personnel may use the first aid kit to administer first aid to any worker who is injured. The HSO shall verify daily those first aid- and CPR-qualified personnel present on site. Unqualified personnel should use the first aid kits to assist in an emergency only when qualified personnel are not available.

9.4 Medical Emergency Procedures

A person certified in first aid, including adult CPR, will be present at all times to render first aid in the event of an injury or illness. For injuries or illness other than very minor cuts or scrapes, a physician's attention is required after first aid is rendered at the site. **For treatment of potentially life-threatening injury or illness, call 911 for assistance**.

For treatment of injuries or illness that can not be easily handled on site with the first aid kit, personnel shall be driven to MidMichigan Urgent Care. Directions to the hospital from the site are indicated on the map provided in Appendix A.

10.0 RESPONSIBILITIES

Project responsibilities are described below.

Project Manager — Will oversee and approve all project activities; review QA reports; approve final project QA needs; authorize necessary actions and adjustments to accomplish program QA objectives; and act as liaison between agencies and field staff.

Quality Assurance (QA) Manager — Will oversee all QA activities to ensure compliance with contract specifications; initiate audits on work completed by project personnel and subcontractors, including analytical laboratories and independent data validation contractors; review program QA activities, quality problems, and quality-related requests. In response to field and analytical findings, he will approve the corrective actions. He will report quality non-conformances to the Project Manager and review all pertinent portions of the deliverables before they are transmitted to ensure conformance with QA/QC procedures and quality work product.

Data Manager — Will oversee data management for this project. He is responsible for the structure, organization, format, implementation, and operation of the project database.

Field Team Leader — Will oversee field activities and supervise the field crews. He will ensure that proper sample collection, preservation, storage, transport, and COC QC procedures are followed. He will inform the Project QA Manager when field problems occur, and will communicate and document corrective actions taken. The Field Team Leader will discuss field activities with the Project Manager.

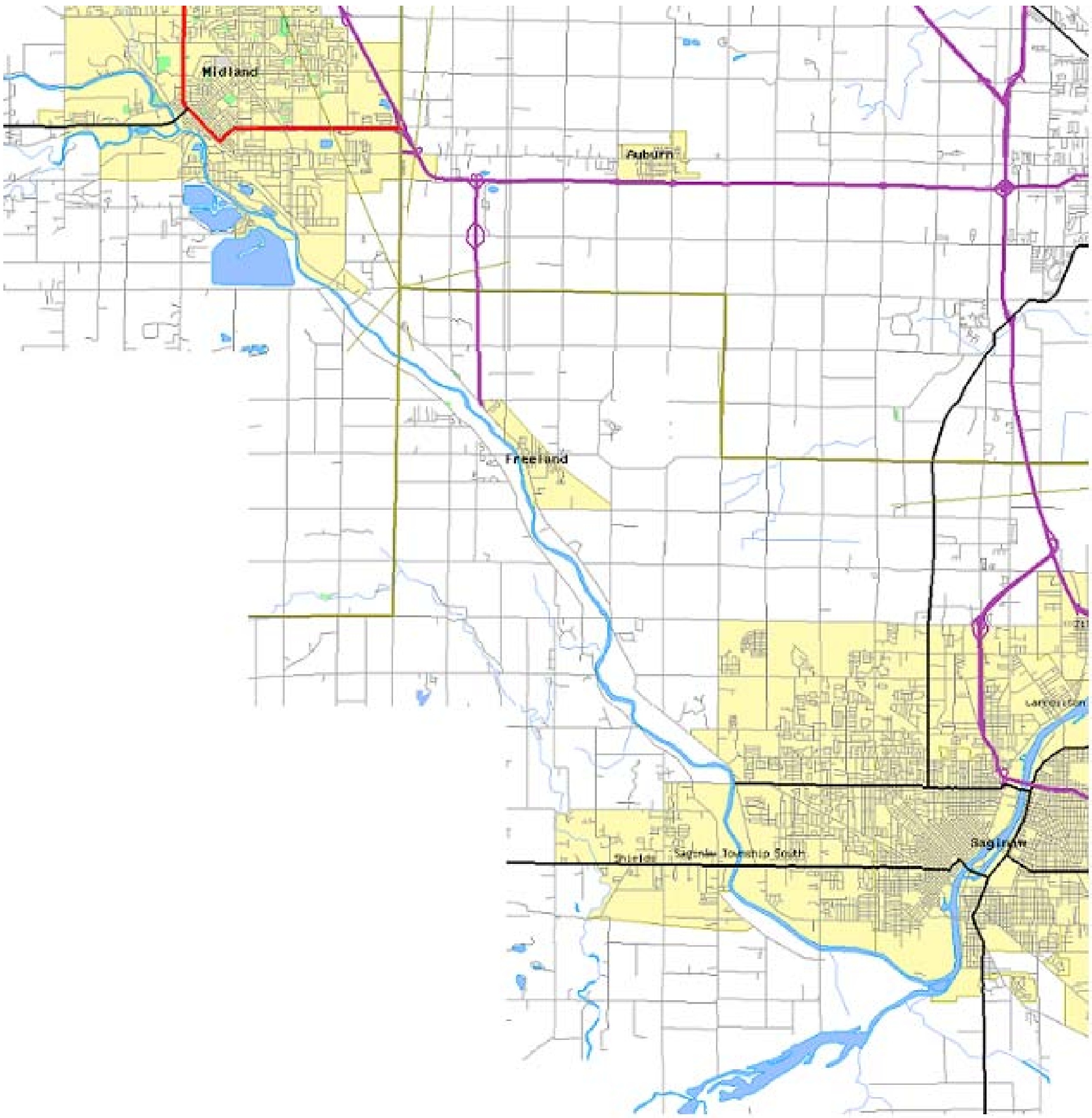
Laboratory Project Manager — The laboratory project manager for this project. He is responsible for assuring that the analysis of all samples is performed in accordance with the QAPP and the laboratory's quality assurance manual. In addition, the Laboratory Project Manager performs the final laboratory review of project data packages for completeness and compliance with project requirements.

Health and Safety Officer — Will oversee the implementation of the site-specific health and safety plan. He will ensure that proper training requirements are fulfilled before field work begins. Incident report forms will be reviewed by the Health and Safety Officer who will have the authority to suspend work or alter procedures at any time to insure the safety of all team members.

APPENDIX A

SITE LOCATION MAP, EMERGENCY CONTACTS, AND HOSPITAL LOCATION MAP

The Tittabawassee River site as defined in the Hazardous Waste Management Facility Operating License (issued on June 12, 2003 by Michigan Department of Environmental Quality to The Dow Chemical Company) includes approximately 23 miles of the Tittabawassee River from the upstream boundry of The Dow Chemical Company to the confluence of the Tittabawassee and Shiawassee Rivers downstream of Greenpoint Island.



Emergency Telephone Numbers

Off site Emergency Contacts

- Fire, Police, Ambulance — 911
- MidMichigan Urgent Care (Midland) — 989-839-1750
- CHEMTREC — 1-800-424-9300
- Poison Control Center — 1-800-662-9886

Additional Contingency Telephone Numbers

- Client Contact: The Dow Chemical Company — 989-636-8897
  Contact: John Phillips

- ENTRIX, Inc., HSO — 517-381-1434 (work)
  Contact: Alan Blankenship — 517-256-2669 (cell)

MidMichigan Urgent Care - Midland
3009 North Saginaw Road
Midland, Michigan 48640 **Telephone**
989-839-1750

APPENDIX B

SITE-SPECIFIC HEALTH AND SAFETY TRAINING RECORD FORMS

SITE-SPECIFIC HEALTH AND SAFETY PLAN (S-HASP) TRAINING RECORD

HASP Title/Revision No. Site-Specific Health and Safety Plan for Field Sampling Activities in Support of the Tittabawassee River Wild Game Workplan; Midland, Michigan

Site Safety Officer	Project Number
________________________________	1092701

I have read the S-HASP listed above and fully understand the material covered. I understand that I am responsible for compliance with the requirements of this S-HASP and I agree to abide by the same. I also had the opportunity to discuss the information presented in the S-HASP, and to ask any questions about the information that I want clarified. I understand that this record will become a permanent part of my employee health and safety training file.

Date	Print Name	Signature

APPENDIX C

TAILGATE SAFETY MEETING FORMS

DAILY TAILGATE SAFETY MEETING FORM

Date:_______________ Time:__________________ Project Number:___1092701________

Project Name:____

Specific Location:____

Type of Work:____

____

Chemicals Present:____

SAFETY TOPICS DISCUSSED

Protective Clothing/Equipment: ____

____

Hazards of Chemicals Present: ____

____

Physical Hazards: ____

____

Special Hazards: ____

____

Other Topics: ____

____

ATTENDEES

Name (printed)	Signature

APPENDIX D

MATERIAL SAFETY DATA SHEETS

ACETONE

1. Product Identification

Synonyms: Dimethylketone; 2-propanone; dimethylketal
CAS No.: 67-64-1
Molecular Weight: 58.08
Chemical Formula: (CH3)2CO
Product Codes:
J.T. Baker: 5008, 5018, 5356, 5580, 9001, 9002, 9003, 9004, 9005, 9006, 9007, 9008, 9009, 9010, 9015, 9036, 9125, 9254, 9271, A134, V655
Mallinckrodt: 0018, 2432, 2435, 2437, 2438, 2440, 2443, 2445, 2850, H451, H580, H981

2. Composition/Information on Ingredients

Ingredient	CAS No	Percent	Hazardous
Acetone	67-64-1	99 - 100%	Yes

3. Hazards Identification

Emergency Overview

DANGER! EXTREMELY FLAMMABLE LIQUID AND VAPOR. VAPOR MAY CAUSE FLASH FIRE. HARMFUL IF SWALLOWED OR INHALED. CAUSES IRRITATION TO SKIN, EYES AND RESPIRATORY TRACT. AFFECTS CENTRAL NERVOUS SYSTEM.

J.T. Baker SAF-T-DATA(tm) Ratings (Provided here for your convenience)

Health Rating: 1 - Slight
Flammability Rating: 4 - Extreme (Flammable)
Reactivity Rating: 2 - Moderate
Contact Rating: 1 - Slight
Lab Protective Equip: GOGGLES; LAB COAT; VENT HOOD; PROPER GLOVES; CLASS B EXTINGUISHER
Storage Color Code: Red (Flammable)

Potential Health Effects

Inhalation:
Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache. Higher concentrations can produce central nervous system depression, narcosis, and unconsciousness.
Ingestion:
Swallowing small amounts is not likely to produce harmful effects. Ingestion of larger amounts may produce abdominal pain, nausea and vomiting. Aspiration into lungs can produce severe lung damage and is a medical emergency. Other symptoms are expected to parallel inhalation.
Skin Contact:
Irritating due to defatting action on skin. Causes redness, pain, drying and cracking of the skin.
Eye Contact:
Vapors are irritating to the eyes. Splashes may cause severe irritation, with stinging, tearing, redness and pain.
Chronic Exposure:
Prolonged or repeated skin contact may produce severe irritation or dermatitis.
Aggravation of Pre-existing Conditions:
Use of alcoholic beverages enhances toxic effects. Exposure may increase the toxic potential of chlorinated hydrocarbons, such as chloroform, trichloroethane.

---

4. First Aid Measures

Inhalation:
Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.
Ingestion:
Aspiration hazard. If swallowed, vomiting may occur spontaneously, but DO NOT INDUCE. If vomiting occurs, keep head below hips to prevent aspiration into lungs. Never give anything by mouth to an unconscious person. Call a physician immediately.
Skin Contact:
Immediately flush skin with plenty of water for at least 15 minutes. Remove contaminated clothing and shoes. Get medical attention. Wash clothing before reuse. Thoroughly clean shoes before reuse.
Eye Contact:
Immediately flush eyes with plenty of water for at least 15 minutes, lifting upper and lower eyelids occasionally. Get medical attention.

---

5. Fire Fighting Measures

Fire:
Flash point: -20C (-4F) CC
Autoignition temperature: 465C (869F)
Flammable limits in air % by volume:
lel: 2.5; uel: 12.8
Extremely Flammable Liquid and Vapor! Vapor may cause flash fire.
Explosion:
Above flash point, vapor-air mixtures are explosive within flammable limits noted above. Vapors can flow along surfaces to distant ignition source and flash back. Contact with strong oxidizers may cause fire. Sealed containers may rupture when heated. This material may produce a floating fire hazard. Sensitive to static discharge.
Fire Extinguishing Media:
Dry chemical, alcohol foam or carbon dioxide. Water may be ineffective. Water spray may be used to keep fire exposed containers cool, dilute spills to nonflammable mixtures, protect personnel attempting to stop leak and disperse vapors.
Special Information:
In the event of a fire, wear full protective clothing and NIOSH-approved self-contained breathing apparatus with full facepiece operated in the pressure demand or other positive pressure mode.

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6. Accidental Release Measures

Ventilate area of leak or spill. Remove all sources of ignition. Wear appropriate personal protective equipment as specified in Section 8. Isolate hazard area. Keep unnecessary and unprotected personnel from entering. Contain and recover liquid when possible. Use non-sparking tools and equipment. Collect liquid in an appropriate container or absorb with an inert material (e. g., vermiculite, dry sand, earth), and place in a chemical waste container. Do not use combustible materials, such as saw dust. Do not flush to sewer! If a leak or spill has not ignited, use water spray to disperse the vapors, to protect personnel attempting to stop leak, and to flush spills away from exposures. US Regulations (CERCLA) require reporting spills and releases to soil, water and air in excess of reportable quantities. The toll free number for the US Coast Guard National Response Center is (800) 424-8802.

J. T. Baker SOLUSORB® solvent adsorbent is recommended for spills of this product.

---

7. Handling and Storage

Protect against physical damage. Store in a cool, dry well-ventilated location, away from any area where the fire hazard may be acute. Outside or detached storage is preferred. Separate from incompatibles. Containers should be bonded and grounded for transfers to avoid static sparks. Storage and use areas should be No Smoking areas. Use non-sparking type tools and equipment, including explosion proof ventilation. Containers of this material may be hazardous when empty since they retain product residues (vapors, liquid); observe all warnings and precautions listed for the product.

---

8. Exposure Controls/Personal Protection

Airborne Exposure Limits:
Acetone:
-OSHA Permissible Exposure Limit (PEL):
1000 ppm (TWA)

-ACGIH Threshold Limit Value (TLV):
500 ppm (TWA), 750 ppm (STEL) A4 - not classifiable as a human carcinogen
Ventilation System:
A system of local and/or general exhaust is recommended to keep employee exposures below the Airborne Exposure Limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, *Industrial Ventilation, A Manual of Recommended Practices*, most recent edition, for details.
Personal Respirators (NIOSH Approved):
If the exposure limit is exceeded, a half-face organic vapor respirator may be worn for up to ten times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. A full-face piece organic vapor respirator may be worn up to 50 times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. For emergencies or instances where the exposure levels are not known, use a full-face piece positive-pressure, air-supplied respirator. WARNING: Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.
Skin Protection:
Wear impervious protective clothing, including boots, gloves, lab coat, apron or coveralls, as appropriate, to prevent skin contact.
Eye Protection:
Use chemical safety goggles and/or a full face shield where splashing is possible. Maintain eye wash fountain and quick-drench facilities in work area.

---

9. Physical and Chemical Properties

Appearance:
Clear, colorless, volatile liquid.
Odor:
Fragrant, mint-like
Solubility:

Miscible in all proportions in water.
Specific Gravity:
0.79 @ 20C/4C
pH:
No information found.
% Volatiles by volume @ 21C (70F):
100
Boiling Point:
56.5C (133F) @ 760 mm Hg
Melting Point:
-95C (-139F)
Vapor Density (Air=1):
2.0
Vapor Pressure (mm Hg):
400 @ 39.5C (104F)
Evaporation Rate (BuAc=1):
ca. 7.7

---

10. Stability and Reactivity

Stability:
Stable under ordinary conditions of use and storage.
Hazardous Decomposition Products:
Carbon dioxide and carbon monoxide may form when heated to decomposition.
Hazardous Polymerization:
Will not occur.
Incompatibilities:
Concentrated nitric and sulfuric acid mixtures, oxidizing materials, chloroform, alkalis, chlorine compounds, acids, potassium t-butoxide.
Conditions to Avoid:
Heat, flames, ignition sources and incompatibles.

---

11. Toxicological Information

Oral rat LD50: 5800 mg/kg; Inhalation rat LC50: 50,100mg/m3; Irritation eye rabbit, Standard Draize, 20 mg severe; investigated as a tumorigen, mutagen, reproductive effector.

--------\Cancer Lists\--

	---NTP Carcinogen---		
Ingredient	Known	Anticipated	IARC Category

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Acetone (67-64-1)	No	No	None

12. Ecological Information

Environmental Fate:
When released into the soil, this material is expected to readily biodegrade. When released into the soil, this material is expected to leach into groundwater. When released into the soil, this material is expected to quickly evaporate. When released into water, this material is expected to readily biodegrade. When released to water, this material is expected to quickly evaporate. This material has a log octanol-water partition coefficient of less than 3.0. This material is not expected to significantly bioaccumulate. When released into the air, this material may be moderately degraded by reaction with photochemically produced hydroxyl radicals. When released into the air, this material may be moderately degraded by photolysis. When released into the air, this material is expected to be readily removed from the atmosphere by wet deposition.
Environmental Toxicity:
This material is not expected to be toxic to aquatic life. The LC50/96-hour values for fish are over 100 mg/l.

13. Disposal Considerations

Whatever cannot be saved for recovery or recycling should be handled as hazardous waste and sent to a RCRA approved incinerator or disposed in a RCRA approved waste facility. Processing, use or contamination of this product may change the waste management options. State and local disposal regulations may differ from federal disposal regulations. Dispose of container and unused contents in accordance with federal, state and local requirements.

14. Transport Information

Domestic (Land, D.O.T.)

Proper Shipping Name: ACETONE
Hazard Class: 3
UN/NA: UN1090
Packing Group: II
Information reported for product/size: 215L

International (Water, I.M.O.)

Proper Shipping Name: ACETONE

Hazard Class: 3
UN/NA: UN1090
Packing Group: II
Information reported for product/size: 215L

---

15. Regulatory Information

--------\Chemical Inventory Status - Part 1\---------------------------------

Ingredient	TSCA	EC	Japan	Australia
Acetone (67-64-1)	Yes	Yes	Yes	Yes

--------\Chemical Inventory Status - Part 2\---------------------------------

Ingredient	Korea	--Canada-- DSL	--Canada-- NDSL	Phil.
Acetone (67-64-1)	Yes	Yes	No	Yes

--------\Federal, State & International Regulations - Part 1\----------------

Ingredient	-SARA 302- RQ	-SARA 302- TPQ	------SARA 313------ List	------SARA 313------ Chemical Catg.
Acetone (67-64-1)	No	No	Yes	No

--------\Federal, State & International Regulations - Part 2\----------------

Ingredient	CERCLA	-RCRA- 261.33	-TSCA- 8(d)
Acetone (67-64-1)	5000	U002	No

Chemical Weapons Convention: No TSCA 12(b): Yes CDTA: Yes

SARA 311/312: Acute: Yes Chronic: No Fire: Yes Pressure: No

Reactivity: No (Pure / Liquid)

Australian Hazchem Code: 2[Y]E
Poison Schedule: None allocated.
WHMIS:
This MSDS has been prepared according to the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all of the information required by the CPR.

---

16. Other Information

NFPA Ratings: Health: 1 Flammability: 3 Reactivity: 0
Label Hazard Warning:
DANGER! EXTREMELY FLAMMABLE LIQUID AND VAPOR. VAPOR MAY CAUSE FLASH FIRE. HARMFUL IF SWALLOWED OR INHALED. CAUSES IRRITATION TO SKIN, EYES AND RESPIRATORY TRACT. AFFECTS CENTRAL NERVOUS SYSTEM.
Label Precautions:
Keep away from heat, sparks and flame.
Keep container closed.
Use only with adequate ventilation.
Wash thoroughly after handling.
Avoid breathing vapor.
Avoid contact with eyes, skin and clothing.
Label First Aid:
Aspiration hazard. If swallowed, vomiting may occur spontaneously, but DO NOT INDUCE. If vomiting occurs, keep head below hips to prevent aspiration into lungs. Never give anything by mouth to an unconscious person. Call a physician immediately. If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes. Remove contaminated clothing and shoes. Wash clothing before reuse. In all cases, get medical attention.
Product Use:
Laboratory Reagent.

Prepared by: Environmental Health & Safety
Phone Number: (314) 654-1600 (U.S.A.)

HEXANES

1. Product Identification

Synonyms: n-Hexane; hexyl hydride; 3-methyl pentane
CAS No.: 110-54-3
Molecular Weight: 86.18
Chemical Formula: CH3(CH2)4CH3 n-hexane
Product Codes: Product Codes: 4153, 4159, 5167, 5175, 5188, 5189, 6969, H079, H487

2. Composition/Information on Ingredients

Ingredient	CAS No	Percent	Hazardous
Hexane	110-54-3	99.4%	Yes

3. Hazards Identification

Emergency Overview

DANGER! EXTREMELY FLAMMABLE LIQUID AND VAPOR. VAPOR MAY CAUSE FLASH FIRE. HARMFUL OR FATAL IF SWALLOWED. HARMFUL IF INHALED OR ABSORBED THROUGH SKIN. CAUSES IRRITATION TO SKIN, EYES AND RESPIRATORY TRACT. AFFECTS THE CENTRAL AND PERIPHERAL NERVOUS SYSTEMS.

SAF-T-DATA(tm) Ratings (Provided here for your convenience)

Health Rating: 3 - Severe (Life)
Flammability Rating: 3 - Severe (Flammable)
Reactivity Rating: 1 - Slight
Contact Rating: 3 - Severe (Life)
Lab Protective Equip: GOGGLES & SHIELD; LAB COAT & APRON; VENT HOOD; PROPER GLOVES; CLASS B EXTINGUISHER
Storage Color Code: Red (Flammable)

Potential Health Effects

The health hazards addressed are for the major component: n-hexane.

Inhalation:
Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Greater exposure may cause muscle weakness, numbness of the extremities, unconsciousness and death.
Ingestion:
May produce abdominal pain, nausea. Aspiration into lungs can produce severe lung damage and is a medical emergency. Other symptoms expected to parallel inhalation.
Skin Contact:
May cause redness, irritation, with dryness, cracking. May be absorbed through the skin with possible systemic effects.
Eye Contact:
Vapors may cause irritation. Splashes may cause redness and pain.
Chronic Exposure:
Repeated or prolonged skin contact may defat the skin and produce irritation and dermatitis. Chronic inhalation may cause peripheral nerve disorders and central nervous system effects.
Aggravation of Pre-existing Conditions:
Persons with pre-existing skin disorders or eye problems or impaired respiratory function may be more susceptible to the effects of the substance. May affect the developing fetus.

---

4. First Aid Measures

Inhalation:
Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.
Ingestion:
Aspiration hazard. If swallowed, vomiting may occur spontaneously, but DO NOT INDUCE. If vomiting occurs, keep head below hips to prevent aspiration into lungs. Never give anything by mouth to an unconscious person. Call a physician immediately.
Skin Contact:
Immediately flush skin with plenty of soap and water for at least 15 minutes while removing contaminated clothing and shoes. Get medical attention. Wash clothing before reuse. Thoroughly clean shoes before reuse.
Eye Contact:
Immediately flush eyes with plenty of water for at least 15 minutes, lifting lower and upper eyelids occasionally. Get medical attention immediately.

Note to Physician:

BEI=2,5-hexadione in urine, sample at end of shift at workweeks end, 5 mg/g creatine. Also, measure n-hexane in expired air. Analgesics may be necessary for pain management, there is no specific antidote. Monitor arterial blood gases in cases of severe aspiration.

---

5. Fire Fighting Measures

Fire:
Flash point: -22C (-8F) CC
Autoignition temperature: 225C (437F)
Flammable limits in air % by volume:
lel: 1.1; uel: 7.5
Listed fire data is for n-Hexane. Extremely Flammable Liquid and Vapor! Vapor may cause flash fire. Dangerous fire hazard when exposed to heat or flame.
Explosion:
Above flash point, vapor-air mixtures are explosive within flammable limits noted above. Contact with oxidizing materials may cause extremely violent combustion.Explodes when mixed @ 28C with dinitrogen tetraoxide. Sensitive to static discharge.
Fire Extinguishing Media:
Dry chemical, foam or carbon dioxide. Water may be ineffective.
Special Information:
In the event of a fire, wear full protective clothing and NIOSH-approved self-contained breathing apparatus with full facepiece operated in the pressure demand or other positive pressure mode. Water spray may be used to keep fire exposed containers cool. Vapors can flow along surfaces to distant ignition source and flash back. Vapor explosion hazard exists indoors, outdoors, or in sewers.

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6. Accidental Release Measures

Ventilate area of leak or spill. Remove all sources of ignition. Wear appropriate personal protective equipment as specified in Section 8. Isolate hazard area. Keep unnecessary and unprotected personnel from entering. Contain and recover liquid when possible. Use non-sparking tools and equipment. Collect liquid in an appropriate container or absorb with an inert material (e. g., vermiculite, dry sand, earth), and place in a chemical waste container. Do not use combustible materials, such as saw dust. Do not flush to sewer! If a leak or spill has not ignited, use water spray to disperse the vapors, to protect personnel attempting to stop leak, and to flush spills away from exposures. US Regulations (CERCLA) require reporting spills and releases to soil, water and air in excess of reportable quantities. The toll free number for the US Coast Guard National Response Center is (800) 424-8802.

---

7. Handling and Storage

Protect against physical damage. Store in a cool, dry well-ventilated location, away from direct sunlight and any area where the fire hazard may be acute. Store in tightly closed containers (preferably under nitrogen atmosphere). Outside or detached storage is preferred. Inside storage should be in a standard flammable liquids storage room or cabinet. Separate from oxidizing materials. Containers should be bonded and grounded for transfers to avoid static sparks. Storage and use areas should be No Smoking areas. Use non-sparking type tools and equipment. Containers of this material may be hazardous when empty since they retain product residues (vapors, liquid); observe all warnings and precautions listed for the product. Do Not attempt to clean empty containers since residue is difficult to remove. Do not pressurize, cut, weld, braze, solder, drill, grind or expose such containers to heat, sparks, flame, static electricity or other sources of ignition: they may explode and cause injury or death.

---

8. Exposure Controls/Personal Protection

Airborne Exposure Limits:
N-Hexane [110-54-3]:
-OSHA Permissible Exposure Limit (PEL): 500 ppm (TWA)
-ACGIH Threshold Limit Value (TLV): 50 ppm (TWA), Skin
other isomers of hexane
-ACGIH Threshold Limit Value (TLV): 500 ppm (TWA),1000ppm (STEL)
Ventilation System:
A system of local and/or general exhaust is recommended to keep employee exposures below the Airborne Exposure Limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, *Industrial Ventilation, A Manual of Recommended Practices*, most recent edition, for details.
Personal Respirators (NIOSH Approved):
If the exposure limit is exceeded and engineering controls are not feasible, wear a supplied air, full-facepiece respirator, airlined hood, or full-facepiece self-contained breathing apparatus. Breathing air quality must meet the requirements of the OSHA respiratory protection standard (29CFR1910.134). This substance has poor warning properties.
Skin Protection:
Wear impervious protective clothing, including boots, gloves, lab coat, apron or coveralls, as appropriate, to prevent skin contact.
Eye Protection:
Use chemical safety goggles and/or a full face shield where splashing is possible. Maintain eye wash fountain and quick-drench facilities in work area.

---

9. Physical and Chemical Properties

Appearance:
Clear, colorless liquid.
Odor:
Gasoline-like odor.
Solubility:
Insoluble in water.
Specific Gravity:
0.664 @ 15.6C/15.6C
pH:
No information found.
% Volatiles by volume @ 21C (70F):
100
Boiling Point:
67 - 69C (153 - 156F)
Melting Point:
No information found.
Vapor Density (Air=1):
ca. 3.0
Vapor Pressure (mm Hg):
No information found.
Evaporation Rate (BuAc=1):
ca. 0.3

---

10. Stability and Reactivity

Stability:
Stable under ordinary conditions of use and storage. Heat will contribute to instability.
Hazardous Decomposition Products:
May produce acrid smoke and irritating fumes when heated to decomposition.
Hazardous Polymerization:
Will not occur.
Incompatibilities:
Strong oxidizers.
Conditions to Avoid:
Heat, flames, ignition sources and incompatibles.

---

11. Toxicological Information

For n-Hexane: LD50 Oral rat 28710 mg/kg; LC50 Inhalation rat 48000 ppm/4H, Irritation eye rabbit (std Draize),10 mg, mild. Investigated as a tumorigen, mutagen and reproductive effector.

--------\Cancer Lists\--

	---NTP Carcinogen---		
Ingredient	Known	Anticipated	IARC Category
Hexane (110-54-3)	No	No	None

12. Ecological Information

Environmental Fate:
When released into the soil, this material may biodegrade to a moderate extent. When released into the soil, this material is not expected to leach into groundwater. When released into the soil, this material is expected to quickly evaporate. When released into water, this material may biodegrade to a moderate extent. When released to water, this material is expected to quickly evaporate. When released into the water, this material is expected to have a half-life between 1 and 10 days. This material has an estimated bioconcentration factor (BCF) of less than 100. This material has a log octanol-water partition coefficient of greater than 3.0. This material is not expected to significantly bioaccumulate. When released into the air, this material is expected to be readily degraded by reaction with photochemically produced hydroxyl radicals. When released into the air, this material is expected to have a half-life between 1 and 10 days.
Environmental Toxicity:
No information found.

13. Disposal Considerations

Whatever cannot be saved for recovery or recycling should be handled as hazardous waste and sent to a RCRA approved incinerator or disposed in a RCRA approved waste facility. Processing, use or contamination of this product may change the waste management options. State and local disposal regulations may differ from federal disposal regulations. Dispose of container and unused contents in accordance with federal, state and local requirements.

14. Transport Information

Domestic (Land, D.O.T.)

Proper Shipping Name: HEXANES
Hazard Class: 3
UN/NA: UN1208
Packing Group: II

DRAFT

Information reported for product/size: 200L

International (Water, I.M.O.)

Proper Shipping Name: HEXANES
Hazard Class: 3
UN/NA: UN1208
Packing Group: II
Information reported for product/size: 200L

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15. Regulatory Information

--------\Chemical Inventory Status - Part 1\---------------------------------

Ingredient	TSCA	EC	Japan	Australia
Hexane (110-54-3)	Yes	Yes	Yes	Yes

--------\Chemical Inventory Status - Part 2\---------------------------------

		--Canada--		
Ingredient	Korea	DSL	NDSL	Phil.
Hexane (110-54-3)	Yes	Yes	No	Yes

--------\Federal, State & International Regulations - Part 1\----------------

	-SARA 302-		------SARA 313------	
Ingredient	RQ	TPQ	List	Chemical Catg.
Hexane (110-54-3)	No	No	Yes	No

--------\Federal, State & International Regulations - Part 2\----------------

		-RCRA-	-TSCA-
Ingredient	CERCLA	261.33	8(d)

Hexane (110-54-3)	5000	No	No

Chemical Weapons Convention: No TSCA 12(b): Yes CDTA: No

SARA 311/312: Acute: Yes Chronic: Yes Fire: Yes Pressure: No

Reactivity: No (Mixture / Liquid)

Australian Hazchem Code: 3[Y]E
Poison Schedule: None allocated.
WHMIS:
This MSDS has been prepared according to the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all of the information required by the CPR.

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16. Other Information

NFPA Ratings: Health: 1 Flammability: 3 Reactivity: 0
Label Hazard Warning:
DANGER! EXTREMELY FLAMMABLE LIQUID AND VAPOR. VAPOR MAY CAUSE FLASH FIRE. HARMFUL OR FATAL IF SWALLOWED. HARMFUL IF INHALED OR ABSORBED THROUGH SKIN. CAUSES IRRITATION TO SKIN, EYES AND RESPIRATORY TRACT. AFFECTS THE CENTRAL AND PERIPHERAL NERVOUS SYSTEMS.
Label Precautions:
Keep away from heat, sparks and flame.
Keep container closed.
Use only with adequate ventilation.
Wash thoroughly after handling.
Avoid breathing vapor or mist.
Avoid contact with eyes, skin and clothing.
Label First Aid:
Aspiration hazard. If swallowed, vomiting may occur spontaneously, but DO NOT INDUCE. If vomiting occurs, keep head below hips to prevent aspiration into lungs. Never give anything by mouth to an unconscious person. Call a physician immediately. If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. In all cases, get medical attention.
Product Use:

Laboratory Reagent.

APPENDIX E

EQUIVALENT CHILL TEMPERATURE

Table E-1. This table shows the cooling power of wind on exposed flesh expressed as equivalent temperature in degrees Fahrenheit under calm conditions.

Wind Speed		Temperature (degrees Fahrenheit)															
mph	kmh	35	30	25	20	15	10	5	0	-5	-10	-15	-20	-25	-30	-35	-40
4	6	35	30	25	20	15	10	5	0	-5	-10	-15	-20	-25	-30	-35	-40
5	8	32	27	22	16	11	6	0	-5	-10	-15	-21	-26	-31	-36	-42	-47
10	16	22	16	10	3	-3	-9	-15	-22	-27	-34	-40	-46	-52	-58	-64	-71
15	24	16	9	2	-5	-11	-18	-25	-31	-38	-45	-51	-58	-65	-72	-78	-85
20	32	12	4	-3	-10	-17	-24	-31	-39	-46	-53	-60	-67	-74	-81	-88	-95
25	40	8	1	-7	-15	-22	-29	-36	-44	-51	-59	-66	-74	-81	-88	-96	-103
30	48	6	-2	-10	-18	-25	-33	-41	-49	-56	-64	-71	-79	-86	-93	-101	-109
35	56	4	-4	-12	-20	-27	-35	-43	-52	-58	-67	-74	-82	-89	-97	-105	-113
40	64	3	-5	-13	-21	-29	-37	-45	-53	-60	-69	-76	-84	-92	-100	-107	-115
45	72	2	-6	-14	-22	-30	-38	-45	-54	-62	-70	-78	-85	-93	-102	-109	-117
		Unpleasant		Frostbite possible		Frostbite likely. Outdoor activity increasingly dangerous.					Exposed flesh will freeze within one-half minute.						

Table E-2. This table shows the cooling power of wind on exposed flesh expressed as equivalent temperature in degrees Celcius under calm conditions.

Wind Speed		Temperature (degrees Celsius)						
km/h	mph	0	-5	-10	-15	-20	-25	-30
10	6	-2	-7	-12	-17	-22	-27	-32
20	12	-7	-13	-19	-25	-31	-37	-43
30	18	-11	-17	-24	-31	-37	-44	-50
40	24	-13	-20	-27	-34	-41	-48	-55
50	30	-15	-22	-29	-36	-44	-51	-58
60	36	-16	-23	-31	-38	-45	-53	-60

APPENDIX F

INCIDENT REPORTING DOCUMENTATION

DRAFT

INCCIDENT/INJURY REPORT

ENTRIX, Inc.

4295 Okemos Rd; Suite 101
Okemos, MI 48864
Ph (517) 381-1434

Type or Print — Police/Fire Emergency Dial 911

TIME & PLACE	Inccident Date:	Time:	
	Location:	Weather:	
DESCRIBE WHAT HAPPENED	Describe What Happened		
INJURED PERSON	Name	Employee # (if applicable)	
	Age:	Gender: Female ☐	Male ☐
	Address		
		PHONE #	
DESCRIPTION OF INJURY	INJURED Yes ☐ No ☐ If Yes - Describe the type, severity, and body part(s) involved: Medical Care Received Yes ☐ No ☐ If Yes - Describe:		
DESCRIPTION OF EQUIPMENT DAMAGE	Describe Equpment Damaged	Cost	
WITNESSES	Name	Address	Phone #
	Name	Address	Phone #

REOCCURRENCE PREVENTION:

Report Completed by: (Print Name & Title) — Date:

Report Reviewed by: (Print Name & Title) — Date:

Appendix D. Standard Operating Procedures (SOP)

SOP #	**Title**
214	Documentation, Preservation, Handling, and Tracking of Samples for Analysis
229	Standard Method for Field Collection of Cottontail Rabbits (*Sylvilagus floridanus*) and Squirrels for Chemical Analyses
230	Protocol for Sampling Wild Turkey (*Meleagris gallopavo*) for Chemical Analyses
231	Standard Method for Field Collection and Processing of White -Tailed Deer (*Odocoileus virginianus*) for Chemical Analyses
401	Sample Management: Receiving, Preservation, Storage, Documentation, Decontamination, and Disposal
402	Maintenance of Sample Integrity, and Proper Usage of Refrigerators, Freezers, and Liquid Nitrogen Dewars
802	Data Package Review

STANDARD OPERATING PROCEDURE

Documentation, Preservation, Handling, And Tracking of Samples For Analysis

Version 2 October 21, 2003

Denise Kay, Ph.D. and Alan Blankenship, Ph.D.

ENTRIX, Inc.

Correspondence to:
4295 Okemos Rd
Okemos, MI 48864
USA
T: (517)-381-1434
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APPROVAL PAGE

Revisions to an existing SOP, addition of an SOP change form, or preparation of a new SOP must be reviewed, approved, and signed by the following:

Authored By: Denise Kay, Ph.D. and Alan Blankenship, Ph.D. Date: 10/21/03

Supervisor Review By: ________________________________ Date: ____________

Reviewed By: ________________________________ Date: ____________
(QA Coordinator)

DEFINITIONS AND ACRONYMS

HASP	Health and Safety Plan
TRAOC	Tittabawassee River Area Of Concern
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure
QA/QC	Quality Assurance, Quality Control
USFWS	United States Fish and Wildlife Service
MDEQ	Michigan Department of Environmental Quality
MDNR	Michigan Department of Natural Resources
PDA	Personal Digital Assistant

TABLE OF CONTENTS

1.0 PURPOSE

The primary purpose of this protocol is to explain the documentation, preservation, handling and tracking of all samples collected from the Tittabawassee River for analysis. This standard operating procedure is intended to address, in detail, all events which could effect tracking, documentation, or integrity of samples so that different sampling personnel can follow these procedures and deliver samples to the laboratory in a reliable and consistent manner.

2.0 SCOPE AND APPLICATION

This procedure describes equipment, field procedures, sample handling, and documentation procedures necessary to properly handle and ship samples for chemical and/or geotechnical analysis from the study area. Specific information regarding sample collection and analysis is found in the Work Plan and in the QAPP.

3.0 SAFETY CONSIDERATIONS

Safety training and medical monitoring requirements are consistent among all protocols for field studies, and are described in the Health and Safety Plan for the Tittabawassee River Field Studies.

4.0 PERMITTING AND NOTIFICATION

Contact the appropriate MDNR, MDEQ, and USFWS offices to fulfill any permitting requirements before commencing fieldwork. A memorandum indicating sampling dates and locations must be sent to the appropriate MDNR, MDQ, and USFWS offices prior to sampling.

5.0 EQUIPMENT, MATERIALS, AND REAGENTS

- Inert packing material
- Sample containers
- Water-proof sample labels
- Chain-of-custody forms
- Custody seals
- Insulated coolers
- Water-proof marking pens
- Shipping tape

- Sealable plastic bags
- Bubble wrap
- Water-proof field logbook
- Ice (wet and dry)
- PDA

6.0 METHOD, PROCEDURES, AND REQUIREMENTS

The following field procedures describe sampling methods in a stepwise fashion and explain the reasoning behind the sampling techniques. Detailed below are the preparatory procedures and sampling objectives.

6.1 Mobilization and Training

This section describes requirements for mobilization for the necessary fieldwork, as well as the appropriate safety training. The objective of this section is to ensure that all of the necessary preparatory work is undertaken to enable the successful completion of the overall project. Mobilization for the necessary fieldwork entails procuring and packing equipment and training field personnel in accordance with the site Health and Safety Plan (HASP). Additional training in proper documentation, label development, and PDA use will be conducted prior to the execution of fieldwork.

The project manager will assemble and pack all equipment specified in the list above. If any items need to be purchased, they will be ordered well in advance to ensure that the schedule is not impacted by equipment needs. Pre-cleaned sample containers will be purchased to minimize the potential for contamination. Finally, sample labels will be printed in advance of fieldwork.

6.2 Objectives

The sampling procedure and plan is designed to maximize confidence in sample integrity. Redundant sampling schemes and sample tracking procedures are used as a precaution to protect sample integrity. All laboratory personnel have been properly trained in these areas and perform these tasks in secured access facilities.

7.0 RECORDS, DOCUMENTATION, AND QC REQUIREMENTS

This section describes records, documentation, and QC requirements, as applicable.

7.1 Sampling Documentation

Field personnel will document all sampling activities in accordance with the Work Plan and sample specific SOPs. During mobilization, sample labels will be pre-printed. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number inserted.

Upon collection, one or more labels will be completed and affixed to the sample container. Just prior to being secured to the sample container in the field, the following information will be added to the label: (a) data and time of collection; (b) temperature and weather conditions; (c) location; and (d) personnel initials. The QA/QC samples will be labeled accordingly. All information from labels will be copied into pre-numbered field notebooks.

7.1.1 Field Identification Number Designations

Each sample label has a unique sample identification number consisting of: a two-letter prefix to distinguish the project ID, a 2-digit number to distinguish location, a two-letter abbreviation for the animal species, and a 2-digit number to designate animal number. In addition, tissue samples will be labeled 'L' or 'M' for liver or muscle, accordingly. Field and laboratory blanks will be labeled with the project ID, date, and type of blank that is being collected. Example ID labeling schemes are illustrated below.

7.1.1.1 Example Animal Sample ID Label

TR01DR01

TR = Tittabawassee River Project
01 = Location
    01 = Reference
    02 = Smith's Crossing
    03 = Imerman Park
DR = Deer; **TY** = Turkey; **RT** = Rabbit; **SL** = Squirrel
01 = Animal number

7.1.1.2 Example Animal Tissue Sample ID Label

TR01DR01L1

TR = Tittabawassee River Project
01 = Location
  01 = Reference
  02 = Smith's Crossing
  03 = Imerman Park
DR = Deer; **TY** = Turkey; **RT** = Rabbit; **SL** = Squirrel
01 = Animal number
L or M = Liver or Muscle tissue
1,2,3… = Replicate tissue sample number

7.1.1.3 Example Blank Sample ID Labels

TR1115BAB01

TR = Tittabawassee River Project
1115 = Date (Month and Day only)
BAB = Blank sample type
  BAB = Butchering Atmospheric Blank
  BSR = Butchering Start Rinsate
  BER = Butchering End Rinsate
  HAB= Homogenate Atmospheric Blank
  HSR = Homogenate Start Rinsate
  HER = Homogenate End Rinsate
01 = Replicate number

7.2 Sample Tracking

Samples collected for analysis will be continuously tracked in the field and in transit to the laboratory. Individual sample bottles will be properly labeled and securely sealed before being placed in the container for shipment to the laboratory. All pertinent information will be entered into the chain-of-custody form in the field. Chain-of-custody forms (Figure 2) include the following: 1) the project name; 2) signatures of samplers; 3) the sample number; 4) date and time of collection; 5) date and time of sample preparation for tissue samples; 6) grab or composite sample designation; 7) signatures of individuals involved in sample transfer; and 8) the air bill or other shipping number, if applicable. The completed chain-of-custody form (Figure 2) will be signed, dated, enclosed in a sealable plastic bag, and placed in the container prior to shipment. Field personnel will retain a copy of the chain-of-custody form and an additional copy transmitted to the CPM or the manager's designee. Samples will be considered in the samplers custody while in sight, or locked in a secure area prior to shipment. All people involved in the handling and packing of the sample will sign the chain-of-custody form. Upon receipt at the laboratory, the designated laboratory sample custodian shall sign the chain-of-custody form indicating receipt of the field samples. The guardian of the samples shall check the actual samples against the chain-of-custody forms upon arrival to the laboratory. The receiving personnel will enter all arriving samples into a laboratory logbook and note any problems or discrepancies and report them immediately to the field sampling coordinator. A copy of the chain-of-custody form shall be returned from the laboratory to the QA/QC officer or designee. The original chain-of-custody shall be retained in the laboratory.

7.3 Sample Containers

All samples will be stored in pre-cleaned containers that are of sufficient size for sample content. All sample jars used are ordered as pre-cleaned and QA/QC grade. If jars are not pre-cleaned and QA/QC grade, then they will be reagent grade acetone and hexane rinsed before use. After the jars have been dried they will be sealed and stored until needed.

7.4 Sample Preservation and Shipping

The samples will be packaged and shipped according to EPA/REAC guidelines (EPA, 1994). To prevent leakage during shipping, sample containers will be no more than 90 percent full. The labeled sample containers, properly sealed and with the exteriors wiped clean and dry, will be placed in a polyethylene bag. The samples will then be placed in an U.S. Department of Transportation (DOT) approved cooler that has been lined with a large polyethylene bag or plastic sheeting. The cooler will be packed with enough noncombustible, absorbent, cushioning material (such as Vermiculite) to minimize the possibility of sample container breakage and to absorb any leaking materials. Because there will be multiple containers per cooler, there will be sufficient cushioning material to prevent breakage if the cooler is dropped or severely shocked. Sufficient dry ice will be placed in each cooler to maintain the necessary temperature throughout the shipping process. One five pound block of dry ice will maintain a temperature below freezing for approximately 24 hours; thus, two blocks will be placed into each shipping container to ensure that the samples will remain frozen for a period of 48 hours. To allow ventilation of the dry ice, coolers with air-tight seals will not be used. The chain-of-custody form will be placed in a watertight bag and taped to the inside of the lid of each cooler. Cooler and box lids will be affixed before shipment, and all containers will be sealed with tape. Samples will be continuously tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures specified in SOP 401 (Sample Management - Receiving, Preservation, Storage, Documentation, Decontamination, and Disposal). Samples will be transported within 48 hours to the Laboratory for processing.

8.0 RESPONSIBILITIES

Project responsibilities are listed below.

Project Manager —Will oversee and approve all project activities; review QA reports; approve final project QA needs; authorize necessary actions and adjustments to accomplish program QA objectives; and act as liaison between agencies and field staff.

Quality Assurance (QA) Manager —Will oversee all QA activities to ensure compliance with contract specifications; initiate audits on work completed by project personnel and subcontractors, including analytical laboratories and independent data validation contractors; review program QA activities, quality problems, and quality-related requests. In response to field and analytical findings, he will approve the corrective actions. He will report quality non-conformances to the Project Manager and review all pertinent portions of the deliverables before they are transmitted to ensure conformance with QA/QC procedures and quality work product.

Data Manager —Will oversee data management for this project. He is responsible for the structure, organization, format, implementation, and operation of the project database.

Field Team Leader — Will oversee field activities and supervise the field crews. He will ensure that proper sample collection, preservation, storage, transport, and COC QC procedures are followed. He will inform the Project QA Manager when field problems occur, and will communicate and document corrective actions taken. The Field Team Leader will discuss field activities with the Project Manager.

Laboratory Project Manager — The laboratory project manager for this project. He is responsible for assuring that the analysis of all samples is performed in accordance with the QAPP and the laboratory's quality assurance manual. In addition, the Laboratory Project Manager performs the final laboratory review of project data packages for completeness and compliance with project requirements.

9.0 REFERENCES

Blasland, Bouck & Lee. 1999. Sampling and Analysis Plan/Data Collection and Analysis Quality

Assurance Plan. Blasland, Bouck & Lee, Inc., Syracuse, NY.

EPA. 1994. Standard Operating Procedures 2004; Sample Packaging and Shipment - EPA/REAC. U.S. Environmental Protection Agency, Washington, DC. U.S. EPA Contract 68-C4-0022. August 11.

Figure 1: Example of a pre-printed label

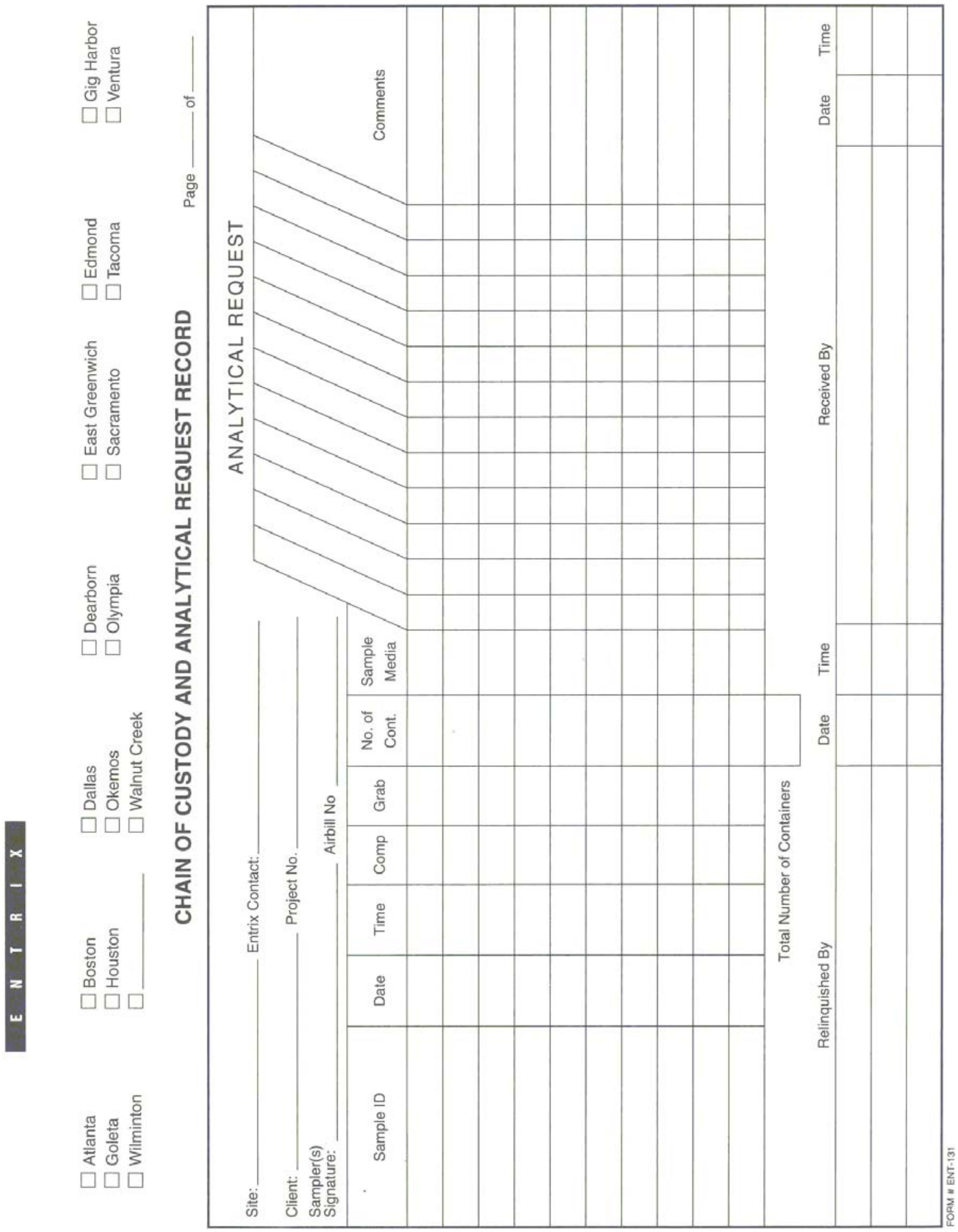
ENTRIX, Inc.
Tittabawassee River Project
SAMPLE ID#:

Date:____________Time:____________Temp/Weather:_______________________
GPS waypoint#: ______________ GPS Position: _________________________

Notes:____

Sampler initials: ________________

Figure 2. Example Chain of Custody Form



ENTRIX

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☐ Wilminton ☐ ______ ☐ Walnut Creek

CHAIN OF CUSTODY AND ANALYTICAL REQUEST RECORD

Page ______ of ______

Site: ______ Entrix Contact: ______
Client: ______ Project No. ______
Sampler(s) Signature: ______ Airbill No ______

Sample ID	Date	Time	Comp	Grab	No. of Cont.	Sample Media	ANALYTICAL REQUEST	Comments

Total Number of Containers

Relinquished By	Date	Time	Received By	Date	Time

FORM # ENT-131

STANDARD OPERATING PROCEDURE

Protocol for Sampling and Analysis of Cottontail Rabbits (*Sylvilagus floridanus*) and Squirrels

Version 1 September 18, 2003

Katherine K. Coady, Ph.D., Patrick Bradley, B.S., and Alan Blankenship, Ph.D.

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APPROVAL PAGE

Revisions to an existing SOP, addition of a SOP change form, or preparation of a new SOP must be reviewed, approved, and signed by the following:

Authored By: Katherine Coady, Ph.D., Patrick Bradley, B.S., and Alan Blankenship, Ph.D. Date: 09/18/03

Supervisor Review By: ______________________________ Date: ____________

Reviewed By: ______________________________ Date: ____________
(QA Coordinator)

DEFINITIONS AND ACRONYMS

MDEQ	Michigan Department of Environmental Quality
MDNR	Michigan Department of Natural Resources
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzofurans
PHAHs	Polyhalogenated aromatic hydrocarbons
QAC	Quality assurance coordinator
SAP	Sampling and Analysis Plan
URCF	University Research and Containment Facility
USFWS	United States Fish and Wildlife Service

TABLE OF CONTENTS

1.0 PURPOSE

The primary purpose of this standard operating procedure (SOP) is to describe the methods that will be used to collect cottontail rabbit and/or squirrel tissue for analysis of congener-specific polyhalogenated aromatic hydrocarbon (PHAH) concentrations. Rabbits and/or squirrels will be collected to address concerns that edible portions of the animals contain concentrations of PHAHs that could pose a risk for human consumption.

Sampling locations are specified in the associated Work Plan. Rabbits and/or squirrels will be collected by standard hunting practices and/or in compliance with state permits. Once rabbits and/or squirrels are collected, select tissue samples will be analyzed individually for lipids and PHAH congeners.

2.0 SCOPE AND APPLICATION

This section describes the species applicability, temporal applicability, and spatial applicability of the methodology described in this protocol.

Cotton-tailed rabbits and/or squirrels will be collected within areas of the floodplain and will be collected just prior to and during the hunting season, so that the sampling effort will coincide and therefore represent normal hunting activities. Every effort will be taken to ensure that collection locations are representative of the area of concern and the hunting activities occurring therein. Analysis of PHAHs will focus on residue concentrations in edible tissues and will indicate the level of contamination in the environment that is available to the hunting public via consumption of rabbits and/or squirrels.

3.0 SAFETY CONSIDERATIONS

Safety training and medical monitoring requirements are consistent among all protocols for field studies, and are described in the Health and Safety Plan for specific field studies.

Use and possession of firearms must be in accordance with all Federal, State, and local laws and regulations. Firearms shall not have a cartridge in the chamber while in a motor vehicle. Firearms left or stored in unattended vehicles must be placed out of public sight and the vehicle locked. Firearms will not be worn, carried, or used in an irresponsible, unsafe, or unprofessional manner. Firearms will not be used if they present a danger to life or property or if a problem with public relations may result. Each employee, regardless of employment status, and official volunteers required or requested to use firearms in conduct of official duties will be provided safety and handling training. Examples of acceptable training would be informal field and/or classroom training conducted by appropriate personnel knowledgeable in firearms safety, self-instructed video training, formal classroom training from firearms professionals, or a combination of each.

4.0 PERMITTING AND NOTIFICATION

Contact the appropriate MDNR, MDEQ and USFWS offices to fulfill any permitting requirements before commencing fieldwork. MDNR, MDEQ and USFWS must be notified of sampling dates and locations prior to sampling.

5.0 EQUIPMENT, MATERIALS, AND REAGENTS

- this SOP
- site Health and Safety Plan
- field sampling checklist
- collecting permits
- detailed site maps
- 2-way radio and/or cell phone
- GPS receiver
- digital camera
- appropriate field clothing (hunter orange if hunting during daylight hours)
- headlamps
- spotlights
- chain of custody forms
- sample labels and sample tags
- duct tape
- packing tape
- 1 field thermometer
- field data documentation forms
- appropriate firearms
- large plastic ziploc bags or garbage bags
- aluminum foil
- gloves
- hunting knives
- knife sharpener
- rain gear
- coolers
- Sharpie waterproof markers
- a waterproof field notebook and clipboard
- chemically-clean glass I-CHEM jars
- top loading balance

- reagent grade acetone and hexane

6.0 METHOD, PROCEDURES, AND REQUIREMENTS

The following field procedures describe the sampling method in a stepwise fashion and explain the reasoning behind the sampling design and techniques. Detailed below are the preparatory procedures, sampling design, sampling techniques, and procedures for sample documentation, preservation, and shipping.

6.1 Mobilization and Training

Mobilization for the necessary fieldwork entails procuring and packing equipment and training of field personnel in accordance with the site Health and Safety Plan (HASP).

The project manager will assemble and pack all equipment specified in the Section above. If any items need to be purchased, they will be ordered well in advance to ensure that the schedule is not impacted by equipment needs. Pre-cleaned sample containers will be purchased to minimize the potential for contamination. Sample labels will be printed in advance of initiating fieldwork.

6.2 Sampling Objectives

The primary objective of the field-sampling portion of this study is to collect a representative sample size of rabbits or squirrels at each sampling location. The target sample size is 10 rabbits or squirrels per sample collection site.

6.3 Sampling Locations

Sampling will occur on the Tittabawasse River floodplain. Two collection sites will be located downstream of Midland, MI and one reference site will be located upstream of Midland, MI. Samples from the downstream locations will be compared to samples collected from the reference location (as specified in the Work Plan).

6.4 Sampling Frequency and Duration

Rabbits and/or squirrels will be sampled from mid to late November. Ideally, rabbits and/or squirrels will be sampled concurrent with other wild game, such as turkey and deer (detailed in SOPs 230 and 231, respectively).

6.5 Field Sampling Methodology

This section details the overall sampling methodology, equipment, and techniques to be employed in this sampling effort.

A. Rabbits and/or squirrels will be collected by standard hunting practices or in compliance with state collecting permits. Authorized personnel will use appropriate firearms to harvest rabbits and/or squirrels.

B. After a harvesting period is complete and an "all-clear" message has been communicated to the field team, the location of each harvested rabbit and/or squirrel will be recorded with coordinates from a global positioning system (GPS). Other environmental parameters, such as time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. Rabbits and/or squirrels will be tagged with pre-printed labels. One sample label will be attached to a hind limb of the rabbit (and/or squirrel) and one sample label will be attached to the bag in which the rabbit (and/or squirrel) carcass is placed.

D. A digital photograph will be taken of the specimen and the GPS unit with coordinates displayed.

E. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: sample number, location, date, time, and collector initials.

F. After placing the rabbit (and/or squirrel) carcass in the appropriate collection bag, the animal will be loaded onto a field vehicle for transport to a nearby field dressing station.

G. Before dressing, rabbit and/or squirrel specimens will be weighed to the nearest ounce and examined for sex classification. Sex will be determined by examining external sex organs and urethral openings. (Males have a rounded, protruding penile sheath with a rounded urethral opening; females have an elongated vulva with a slit opening.)

H. Weight and sex of the rabbits and/or squirrels will be recorded in the appropriate field laboratory notebook.

I. Rabbits and/or squirrels will be dressed according to standard hunting practices, except that all surfaces and instruments that might contact the samples will be rinsed with reagent grade acetone/hexane before each rabbit is dressed.

J. All edible portions of the muscle tissue will be removed from each rabbit and/or squirrel. Specifically, muscle tissue will be removed from the legs and torso of collected specimens. The collective muscle tissue weight will be recorded in the field notebook.

K. All muscle samples will be cut into approximately 1" cubes and then placed in pre-labeled, chemically clean I-CHEM jars (500 or 1000 ml capacity).

L. Muscle samples in I-CHEM jars will be immediately placed on ice as described below in section 6.6.

M. The remainder of each carcass will be placed in a plastic bag and stored frozen until the end of the study.

6.6 Sample Preservation and Transport

A secure freezer trailer unit will be used for temporary storage of rabbit and/or squirrel carcasses at the field dressing location. Long term storage of rabbit and/or squirrel carcasses (until study termination) will take place at an off-site storage location yet to be determined. Tissue samples (in I-CHEM jars) will be immediately placed in ice-filled coolers and will be transported to the University Research and Containment Facility (URCF) at Michigan State University where they will be stored at –20°C until homogenization. All samples will be continuously tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures specified in SOP 401 (Sample Management - Receiving, Preservation, Storage, Documentation, Decontamination, and Disposal).

6.7 Laboratory Sample Preparation

A. Tissue samples will be stored at –20°C until they are ready for homogenization.

B. Tissues will be homogenized in stainless steel blenders. In between samples, blenders will be washed with Liquinox soap, rinsed 3 times with nanopure water, and reagent grade acetone and hexane rinsed.

C. Homogenates will be aliquoted into six separate chemically clean I-CHEM jars. One jar will be shipped to each analytical laboratory, while any remaining jars will be archived at the URCF. Sample IDs will be labeled for each replicate homogenate sample as described in SOP (Documentation, Preservation, Handling, and Tracking of Samples for Analysis).

D. All tissue homogenates will be stored in the -20° C freezer until time of shipment to the analytical laboratory.

E. All laboratory practices will be recorded in the appropriate laboratory notebook.

6.8 Sample Shipping to Analytical Laboratory

Tissue homogenates will be packaged and shipped for analysis according to EPA/REAC guidelines (EPA, 1994). Samples will be shipped in coolers on ice. To prevent leakage during shipping, sample containers will be no more than 90 percent full. The labeled sample containers properly sealed and with the exteriors wiped clean and dry, will be placed in a polyethylene bag. The samples will then be placed in an U.S. Department of Transportation (DOT) approved cooler that has been lined with a large polyethylene bag or plastic sheeting. Because there will be multiple containers per cooler, there will be sufficient cushioning material between them to prevent breakage if the cooler is dropped or severely shocked. One chain-of-custody form will be placed in a watertight bag and taped to the inside of the lid of each cooler. Cooler and box lids will be affixed before shipment, and all containers will be sealed with tape. Coolers will be sealed with signed custody seals prior to shipment.

7.0 RECORDS, DOCUMENTATION, AND QC REQUIREMENTS

This section describes records, documentation, and QC requirements, as applicable.

7.1 Sampling Documentation

For each individual caught, the following observations and measurements will be recorded:

- species
- date collected
- site location and GPS coordinates
- sex
- type of tissues collected
- weight of all tissue collected
- collectors initials

During mobilization, sample labels will be pre-printed with the project name and a unique sample identification number. Just prior to being secured to the sample container in the field, the following information will be added to the label: (a) data and time of collection; (b) temperature and weather conditions; (c) location; and (d) personnel initials. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number inserted. The QA/QC samples will be labeled accordingly. Detailed procedures for sample labeling are addressed in SOP 214 (Documentation, Preservation, Handling, and Tracking of Samples for Analysis).

7.2 Quality Assurance

Field blanks and field duplicates will be used to monitor for sampling errors, interferences, and/or contamination that might occur as a result of field sample collection, packaging, or shipping. A field blank will consist of clean sodium sulfate that is prepared, stored, and analyzed for PHAH congeners as if it were an actual sample. This meets EPA's stipulation that field blanks should be submitted at a rate of five percent of the total number of samples. Additionally, two other biota samples will be needed to perform matrix spike/matrix spike duplicate (MS/MSD) analyses. The matrix spikes for rabbit and/or squirrel samples will consist of muscle homogenates spiked with known concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and 2,3,7,8-tetrachlorodibenzofuran.

7.3 Data Evaluation

Once results of the laboratory analyses have been completed, the average concentrations of PHAH congeners across sampling locations will be calculated. This process, and the subsequent data evaluation, is detailed in the following sections on data compilation, statistical analyses of the results and documentation of the procedure and results.

7.4 Data Compilation

The initial step in data evaluation will be to review the laboratory reports and data sheets for completeness and qualifiers. All of the sampling information will be compiled in a spreadsheet. The following information will be included: sampling ID number, sampling location, date and time of sample collection, names of taxa represented in biotic samples by fraction mass, lipid content of tissues, and PHAH congener concentrations of tissues. The accuracy of the above data entry will be verified by a scientist other than the one that entered the data. The results of the QA/QC samples (field blanks MS, MSD) will be considered to detect possible sources of interference or contamination.

7.5 Statistical Analysis

The objectives of statistical analysis are to: (a) identify and report the PHAH congener concentrations measured in rabbits and/or squirrels that have been collected from the study area; (b) calculate summary statistics; (c) evaluate differences in total PHAH concentrations between study and reference sites; and (d) calculate the potential risk of PHAH exposure to humans.

As an initial step in the statistical analysis of rabbit and/or squirrel analytical results, summary statistics will include the range, arithmetic mean, 95 percent confidence limits on the mean, median, geometric mean, standard deviation, and standard error. One-half of the detection limit will be substituted for any non-detect concentrations.

7.6 Schedule

Rabbit and/or squirrel sampling will begin mid-November of 2003 and end by late November 2003. Rabbit and/or squirrel necropsy as well as tissue collection and homogenization will take place throughout the months of November and December. PHAH analyses will initiate as soon as possible and it is expected that data will be summarized by March 2004.

8.0 RESPONSIBILITIES

Project responsibilities are listed below.

Project Manager —Will oversee and approve all project activities; review QA reports; approve final project QA needs; authorize necessary actions and adjustments to accomplish program QA objectives; and act as liaison between agencies and field staff.

Quality Assurance (QA) Manager —Will oversee all QA activities to ensure compliance with contract specifications; initiate audits on work completed by project personnel and subcontractors, including analytical laboratories and independent data validation contractors; review program QA activities, quality problems, and quality-related requests. In response to field and analytical findings, he will approve the corrective actions. He will report quality non-conformances to the Project Manager and review all pertinent portions of the deliverables before they are transmitted to ensure conformance with QA/QC procedures and quality work product.

Data Manager —Will oversee data management for this project. He is responsible for the structure, organization, format, implementation, and operation of the project database.

Field Team Leader — Will oversee field activities and supervise the field crews. He will ensure that proper sample collection, preservation, storage, transport, and COC QC procedures are followed. He will inform the Project QA Manager when field problems occur, and will communicate and document corrective actions taken. The Field Team Leader will discuss field activities with the Project Manager.

Laboratory Project Manager — The laboratory project manager for this project. He is responsible for assuring that the analysis of all samples is performed in accordance with the QAPP and the laboratory's quality assurance manual. In addition, the Laboratory Project Manager performs the final laboratory review of project data packages for completeness and compliance with project requirements.

9.0 REFERENCES

EPA. (1994). Standard Operating Procedures 2004; Sample Packaging and Shipment - EPA/REAC. U.S. Environmental Protection Agency, Washington, DC. U.S. EPA Contract 68-C4-0022. August 11.

STANDARD OPERATING PROCEDURE

Protocol for Sampling and Analysis of Wild Turkey (*Meleagris gallopavo*)

Version 1 September 18, 2003

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APPROVAL PAGE

Revisions to an existing SOP, addition of a SOP change form, or preparation of a new SOP must be reviewed, approved, and signed by the following:

Authored By: Katherine Coady, Ph.D., Patrick Bradley, B.S., and Alan Blankenship, Ph.D. Date: 09/18/03

Supervisor Review By: ______________________________ Date: ____________

Reviewed By: ______________________________ Date: ____________
(QA Coordinator)

DEFINITIONS AND ACRONYMS

MDEQ	Michigan Department of Environmental Quality
MDNR	Michigan Department of Natural Resources
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzofurans
PHAHs	Polyhalogenated aromatic hydrocarbons
QAC	Quality assurance coordinator
SAP	Sampling and Analysis Plan
URCF	University Research and Containment Facility
USFWS	United States Fish and Wildlife Service

TABLE OF CONTENTS

1.0 PURPOSE

The primary purpose of this standard operating procedure (SOP) is to describe the methods that will be used to collect wild turkey tissue for analysis of congener-specific polyhalogenated aromatic hydrocarbon (PHAH) concentrations. Wild turkey will be collected to address concerns that edible portions of the animals contain concentrations of PHAHs that could pose a risk for human consumption.

Sampling locations are specified in the associated Work Plan. Wild turkey will be collected by standard hunting practices and/or in compliance with state permits. Once turkey are collected, select tissue samples will be analyzed individually for lipids and PHAH congeners.

2.0 SCOPE AND APPLICATION

This section describes the species applicability, temporal applicability, and spatial applicability of the methodology described in this protocol.

Wild turkey will be collected within areas of the floodplain. In addition, turkey will be collected just prior to and during the hunting season, so that the sampling effort will coincide and therefore represent normal hunting activities. Thus, the collection will be representative of the area of concern and the hunting activities occurring therein. Analysis of PHAHs will focus on residue concentrations in edible tissues and will indicate the level of contamination in the environment that is available to the hunting public via consumption of turkey.

3.0 SAFETY CONSIDERATIONS

Safety training and medical monitoring requirements are consistent among all protocols for field studies, and are described in the Health and Safety Plan for specific field studies.

Use and possession of firearms must be in accordance with all Federal, State, and local laws and regulations. Firearms shall not have a cartridge in the chamber while in a motor vehicle. Firearms left or stored in unattended vehicles must be placed out of public sight and the vehicle locked. Firearms will not be worn, carried, or used in an irresponsible, unsafe, or unprofessional manner. Firearms will not be used if they present a danger to life or property or if a problem with public relations may result. Each employee, regardless of employment status, and official volunteers required or requested to use firearms in conduct of official duties will be provided safety and handling training. Examples of acceptable training would be informal field and/or classroom training conducted by appropriate personnel knowledgeable in firearm safety, self-instructed video training, formal classroom training from firearms professionals, or a combination of each.

4.0 PERMITTING AND NOTIFICATION

Contact the appropriate MDNR, MDEQ and USFWS offices to fulfill any permitting requirements before commencing fieldwork. MDNR, MDEQ and USFWS must be notified of sampling dates and locations prior to sampling.

5.0 EQUIPMENT, MATERIALS, AND REAGENTS

- this SOP
- site Health and Safety Plan
- field sampling checklist
- collecting permits
- detailed site maps
- 2-way radio and/or cell phone
- GPS receiver
- digital camera
- appropriate field clothing (hunter orange if hunting during daylight hours)
- headlamps
- spotlights
- chain of custody forms
- sample labels and sample tags
- duct tape
- packing tape
- 1 field thermometer
- field data documentation forms
- appropriate firearms
- large plastic ziploc bags or garbage bags
- gloves
- hunting knives
- knife sharpener
- turkey plucker
- rain gear
- coolers
- Sharpie waterproof markers
- a waterproof field notebook and clipboard
- chemically-clean glass I-CHEM jars
- top loading balance
- reagent grade acetone and hexane

6.0 METHOD, PROCEDURES, AND REQUIREMENTS

The following field procedures describe the sampling method in a stepwise fashion and explain the reasoning behind the sampling design and techniques. Detailed below are the preparatory procedures, sampling design, sampling techniques, and procedures for sample documentation, preservation, and shipping.

6.1 Mobilization and Training

Mobilization for the necessary fieldwork entails procuring and packing equipment, and training of field personnel in accordance with the site Health and Safety Plan (HASP).

The project manager will assemble and pack all equipment specified in the Section above. If any items need to be purchased, they will be ordered well in advance to ensure that the schedule is not impacted by equipment needs. Pre-cleaned sample containers will be purchased to minimize the potential for contamination. Sample labels will be printed in advance of initiating fieldwork.

6.2 Sampling Objectives

The primary objective of the field-sampling portion of this study is to collect a representative sample size of both male and female wild turkey at each sampling location. The target sample size is 10 turkeys per sample collection site.

6.3 Sampling Locations

Sampling will occur on the Tittabawasse River floodplain. Two collection sites will be located downstream of Midland, MI and one reference site will be located upstream of Midland, MI. Samples from the downstream locations will be compared to samples collected from the reference location (as specified in the Work Plan).

6.4 Sampling Frequency and Duration

Wild turkey will be sampled from mid to late November. Ideally, turkeys will be sampled concurrent with other wild game, such as deer and rabbits (detailed in SOP 231 and 229, respectively).

6.5 Field Sampling Methodology

This section details the overall sampling methodology, equipment, and techniques to be employed in this sampling effort.

A. Wild turkey will be collected by standard hunting practices or in compliance with state collecting permits. Authorized personnel will use appropriate firearms to harvest turkey.

B. After a harvesting period is complete and an "all-clear" message has been communicated to the field team, the location of each harvested turkey will be recorded with coordinates from a global positioning system (GPS). Other environmental parameters, such as time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. Turkeys will be tagged with pre-printed sample labels. One sample label will be attached to a limb of the turkey and one sample label will be attached to the bag in which the turkey carcass is placed.

D. A digital photograph will be taken of the specimen and the GPS unit with coordinates displayed.

E. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: location, date, time and collector initials.

F. After placing the turkey carcass in the appropriate collection bag, the animal will be loaded onto a field vehicle for transport to a nearby field dressing station.

G. Before dressing, turkeys will be weighed to the nearest ounce and examined for sex classification. Sex will be determined by examining the breast feathers of the turkeys. (The feathers of the hen are rounded and buff colored while the feathers of the gobbler are squamate and black-tipped.) Sex of the turkeys may also be determined by the relatively greater height of the gobbler and the presence or absence of a beard or spur.

H. Weight and sex of the turkeys will be recorded in the appropriate field laboratory notebook.

I. Turkeys will be dressed according to standard hunting practices, except that all surfaces and instruments which might contact the samples will be rinsed with reagent grade acetone/hexane before the turkey is dressed. An automatic turkey plucker will be used to dress the turkeys.

J. Edible portions of the muscle tissue will be removed from the turkey. Specifically, muscle tissue will be removed from the chest and leg regions of the turkey. Approximately 700g of white meat will be removed from the breast, and approximately 300 g of dark meat will be removed from the legs.

K. All muscle samples will be cut into approximately 1" cubes. For each muscle/meat group, the cubes will be transferred to a weighing boat until the target weight is approached. The last cube to be added will be trimmed until the target weight is achieved as close as possible. The actual weights for each muscle/meat group will be recorded and then transferred into a single chemically clean, 1000-mL I-Chem jar.

L. Turkey muscle samples in I-CHEM jars will be immediately placed on ice as described below in section 6.6.

M. The remainder of each carcass will be placed in a plastic bag and stored frozen until the end of the study.

6.6 Sample Preservation and Transport

A secure freezer trailer unit will be used for temporary storage of turkey carcasses at the field dressing location. Long term storage of turkey carcasses (until study termination) will take place at an off-site storage location yet to be determined. Tissue samples (in I-CHEM jars) will be immediately placed in ice-filled coolers and be transported to the University Research and Containment Facility (URCF) at Michigan State University where they will be stored at –20°C until homogenization. All samples will be continuously tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures specified in SOP 401 (Sample Management - Receiving, Preservation, Storage, Documentation, Decontamination, and Disposal).

6.7 Laboratory Sample Preparation

A. Tissue samples will be stored at –20°C until they are ready for homogenization.

B. Tissues will be homogenized in stainless steel blenders. In between samples, blenders will be washed with Liquinox soap, rinsed 3 times with nanopure water, and reagent grade acetone and hexane rinsed.

C. Homogenates will be aliquoted into six separate chemically clean I-CHEM jars. One jar will be shipped to each analytical laboratory, while any remaining jars will be archived at the URCF. Sample IDs will be labeled for each replicate homogenate sample as described in SOP 214 (Documentation, Preservation, Handling, and Tracking of Samples for Analysis).

D. All tissue homogenates will be stored in the -20° C freezer until time of shipment to the analytical laboratory.

E. All laboratory practices will be recorded in the appropriate laboratory notebook.

6.8 Sample Shipping to Analytical Laboratory

Tissue homogenates will be packaged and shipped for analysis according to EPA/REAC guidelines (EPA, 1994). Samples will be shipped in coolers on ice. To prevent leakage during shipping, sample containers will be no more than 90 percent full. The labeled sample containers properly sealed and with the exteriors wiped clean and dry, will be placed in a polyethylene bag. The samples will then be placed in an U.S. Department of Transportation (DOT) approved cooler that has been lined with a large polyethylene bag or plastic sheeting. Because there will be multiple containers per cooler, there will be sufficient cushioning material between them to prevent breakage if the cooler is dropped or severely shocked. One chain-of-custody form will be placed in a watertight bag and taped to the inside of the lid of each cooler. Cooler and box lids will be affixed before shipment, and all containers will be sealed with tape. Coolers will be sealed with signed custody seals prior to shipment.

7.0 RECORDS, DOCUMENTATION, AND QC REQUIREMENTS

This section describes records, documentation, and QC requirements, as applicable.

7.1 Sampling Documentation

For each individual caught, the following observations and measurements will be recorded:

- species
- date collected
- site location and GPS coordinates
- sex
- type of all tissues collected (e.g. breast muscle, leg muscle)
- weight of all tissue collected
- collectors initials

During mobilization, sample labels will be pre-printed with the project name and a unique sample identification number. Just prior to being secured to the sample container in the field, the following information will be added to the label: (a) data and time of collection; (b) temperature and weather conditions; (c) location; and (d) personnel initials. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number inserted. The QA/QC samples will be labeled accordingly. Detailed procedures for sample labeling is addressed in SOP 214 (Documentation, Preservation, Handling, and Tracking of Samples for Analysis).

7.2 Quality Assurance

Field blanks and field duplicates will be used to monitor for sampling errors, interferences, and/or contamination that might occur as a result of field sample collection, packaging, or shipping. A field blank will consist of clean sodium sulfate that is prepared, stored, and analyzed for PHAH congeners as if it were an actual sample. This meets EPA's stipulation that field blanks should be submitted at a rate of five percent of the total number of samples. Additionally, two other biota samples will be needed to perform matrix spike/matrix spike duplicate (MS/MSD) analyses. The matrix spikes for turkey samples will consist of muscle homogenates spiked with known concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and 2,3,7,8-tetrachlorodibenzofuran.

7.3 Data Evaluation

Once results of the laboratory analyses have been completed, the average concentrations of PHAH congeners across sampling locations will be calculated. This process, and the subsequent data evaluation, is detailed in the following sections on data compilation, statistical analyses of the results and documentation of the procedure and results.

7.4 Data Compilation

The initial step in data evaluation will be to review the laboratory reports and data sheets for completeness and qualifiers. All of the sampling information will be compiled in a spreadsheet. The following information will be included: sampling ID number, sampling location, date and time of sample collection, names of taxa represented in biotic samples by fraction mass, lipid content of tissues, and PHAH congener concentrations of tissues. The accuracy of the above data entry will be verified by a scientist other than the one that entered the data. The result of the QA/QC samples (field blanks, MS, MSD) will be considered to detect possible sources of interference or contamination.

7.5 Statistical Analysis

The objectives of statistical analysis are to: (a) identify and report the PHAH congener concentrations measured in wild turkey that have been collected from the study area; (b) calculate summary statistics; (c) evaluate differences in total PHAH concentrations between study and reference sites; and (d) calculate the potential risk of PHAH exposure to humans.

As an initial step in the statistical analysis of wild turkey analytical results, summary statistics will include the range, arithmetic mean, 95 percent confidence limits on the mean, median, geometric mean, standard deviation, and standard error. One-half of the detection limit will be substituted for any non-detect concentrations.

7.6 Schedule

Turkey sampling will begin mid-November of 2003 and end by late November 2003. Turkey processing as well as tissue collection and homogenization will take place throughout the months of November and December. PHAH analyses will initiate as soon as possible and it is expected that data will be summarized by March 2004.

8.0 RESPONSIBILITIES

Project responsibilities are listed below.

Project Manager —Will oversee and approve all project activities; review QA reports; approve final project QA needs; authorize necessary actions and adjustments to accomplish program QA objectives; and act as liaison between agencies and field staff.

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Data Manager —Will oversee data management for this project. He is responsible for the structure, organization, format, implementation, and operation of the project database.

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Laboratory Project Manager — The laboratory project manager for this project. He is responsible for assuring that the analysis of all samples is performed in accordance with the QAPP and the laboratory's quality assurance manual. In addition, the Laboratory Project Manager performs the final laboratory review of project data packages for completeness and compliance with project requirements.

9.0 REFERENCES

EPA. (1994). Standard Operating Procedures 2004; Sample Packaging and Shipment - EPA/REAC. U.S. Environmental Protection Agency, Washington, DC. U.S. EPA Contract 68-C4-0022. August 11.

STANDARD OPERATING PROCEDURE

Protocol for Field Sampling White -Tailed Deer (*Odocoileus virginianus*)

Version 1 September 18, 2003

Katherine K. Coady, Ph.D., Patrick Bradley, B.S., and Alan Blankenship, Ph.D.

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APPROVAL PAGE

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Authored By: Katherine Coady, Ph.D., Patrick Bradley, B.S., and Alan Blankenship, Ph.D. Date: 09/18/03

Supervisor Review By: ______________________________ Date: ____________

Reviewed By: ______________________________ Date: ____________
(QA Coordinator)

DEFINITIONS AND ACRONYMS

MDEQ	Michigan Department of Environmental Quality
MDNR	Michigan Department of Natural Resources
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzofurans
PHAHs	Polyhalogenated aromatic hydrocarbons
QAC	Quality assurance coordinator
SAP	Sampling and Analysis Plan
URCF	University Research and Containment Facility
USFWS	United States Fish and Wildlife Service

TABLE OF CONTENTS

1.0 PURPOSE

The primary purpose of this standard operating procedure (SOP) is to describe the methods that will be used to collect white-tailed deer tissue for analysis of congener-specific polyhalogenated aromatic hydrocarbon (PHAH) concentrations in select tissue samples. Deer will be collected to address concerns that edible portions of the animals contain concentrations of PHAHs that could pose a risk for human consumption.

Sampling locations are specified in the associated Work Plan. White-tailed deer will be collected by standard hunting practices and/ or in compliance with state permits. Once deer are collected, select tissue samples will be analyzed individually for lipids and PHAH congeners.

2.0 SCOPE AND APPLICATION

This section describes the species applicability, temporal applicability, and spatial applicability of the methodology described in this protocol.

White-tailed deer will be collected within areas of the Tittabawassee River floodplain and will be collected just prior to and during the hunting season, so that the sampling effort will coincide and therefore represent normal hunting activities. Analysis of PHAHs will focus on residue concentrations in edible deer tissue and will indicate the level of contamination in the environment that is available to the hunting public via consumption of venison.

3.0 SAFETY CONSIDERATIONS

Safety training and medical monitoring requirements are consistent among all protocols for field studies, and are described in the Health and Safety Plan for specific field studies.

Use and possession of firearms must be in accordance with all Federal, State, and local laws and regulations. Firearms shall not have a cartridge in the chamber while in a motor vehicle. Firearms left or stored in unattended vehicles must be placed out of public sight and the vehicle locked. Firearms will not be worn, carried, or used in an irresponsible, unsafe, or unprofessional manner. Firearms will not be used if they present a danger to life or property or if a problem with public relations may result. Each employee, regardless of employment status, and official volunteers required or requested to use firearms in conduct of official duties will be provided safety and handling training. Examples of acceptable training would be informal field and/or classroom training conducted by appropriate personnel knowledgeable in firearm safety, self-instructed video training, formal classroom training from firearms professionals, or a combination of each.

4.0 PERMITTING AND NOTIFICATION

Contact the appropriate MDNR, MDEQ, and USFWS offices to fulfill any permitting requirements before commencing fieldwork. MDNR, MDEQ and USFWS must be notified of sampling dates and locations prior to sampling.

5.0 EQUIPMENT, MATERIALS, AND REAGENTS

- this SOP
- site Health and Safety Plan
- field sampling checklist
- collecting permits
- detailed site maps
- 2-way radio and/or cell phone
- GPS receiver
- digital camera
- appropriate field clothing (hunter orange if hunting during daylight hours)
- headlamps
- spotlights
- chain of custody forms
- sample labels and sample tags
- duct tape
- garbage bags
- packing tape
- 1 field thermometer
- field data documentation forms
- appropriate firearms
- plastic sheeting
- large plastic ziploc bags
- aluminum foil
- gloves
- sawzall electric saw
- hunting knives
- knife sharpener
- absorbent pads
- masks
- goggles
- disposable lab coat
- rain gear
- coolers

- sharpie waterproof markers
- a waterproof field notebook and clipboard
- chemically clean glass I-CHEM jars (1000, 500, 250 ml capacity)
- top loading balance
- mops
- bleach
- rope
- gambrel
- hoist
- reagent grade acetone and hexane

6.0 METHOD, PROCEDURES, AND REQUIREMENTS

The following field procedures describe the sampling method in a stepwise fashion and explain the reasoning behind the sampling design and techniques. Detailed below are the preparatory procedures, sampling design, sampling techniques, and procedures for sample documentation, preservation, and shipping.

6.1 Mobilization and Training

Mobilization for the necessary fieldwork entails procuring and packing equipment and training of field personnel in accordance with the site Health and Safety Plan (HASP).

The project manager will assemble and pack all equipment specified in the Section above. If any items need to be purchased, they will be ordered well in advance to ensure that the schedule is not impacted by equipment needs. Pre-cleaned sample containers will be purchased to minimize the potential for contamination. Sample labels will be printed in advance of initiating fieldwork.

6.2 Sampling Objectives

The primary objective of the field-sampling portion of this study is to collect a representative sample size of both male and female white-tailed deer at each sampling location. Target sample sizes are 10-15 deer per study site.

6.3 Sampling Locations

Sampling will occur on the Tittabawasse River floodplain. Two collection sites will be located downstream of Midland, MI and one reference site will be located upstream of Midland, MI. Samples from the downstream locations will be compared to samples collected from the reference location (as specified in the Work Plan).

6.4 Sampling Frequency and Duration

White-tailed deer will be sampled from mid to late November. In order to easily locate and harvest the deer, most sampling will occur at night with the use of spotlights.

6.5 Field Sampling Methodology

This section details the overall sampling methodology, equipment, and techniques to be employed in this sampling effort.

A. White-tailed deer will be collected by standard hunting practices or in compliance with state collecting permits. Authorized personnel will use appropriate firearms to harvest deer.

B. After a harvesting period is complete and an "all-clear" message has been communicated to the field team, the location of each harvested deer will be recorded with coordinates from a global positioning system (GPS). Other environmental parameters, such as time, temperature, or weather conditions, will also be recorded on sample labels and in the field notebook as deemed necessary.

C. Deer will be tagged with pre-printed labels. One sample label will be attached to the ear of the deer and the other attached on one of the hind limbs.

D. A digital photograph will be taken of the specimen and the GPS unit with coordinates displayed.

E. The torso of the deer will be wrapped in plastic sheeting. Sample labels will be recorded in the field notebook and attached to the back of each of the sample tags. Each sample label will include the following information: location, date, time, and collector initials.

F. After wrapping the deer in plastic sheeting, the carcass will be loaded onto a field vehicle for transport to a nearby location for field dressing.

G. Deer will be dressed according to standard hunting practices, except that all surfaces and instruments that might contact the samples will be rinsed with reagent grade acetone and hexane before each deer is dressed.

H. The entire liver will be removed, weighed and then rinsed with nanopure water to remove any foreign debris and/or fur that may have come into contact with the tissue during field dressing. Approximately 1000 g of liver tissue will be cut into approximately 1" cubes and transferred to a 1000 ml glass I-CHEM jar that is chemically clean and pre-labeled.

I. After skinning, edible portions of muscle will be cut away from the rump roast area, tenderloin area, and backstrap area. Each of these muscle/meat groups will be cut into small cubes (approximately 1 cubic inch). The target weights are 500 g of rump roast, 250 g of tenderloin, and 250 g of backstrap. For each muscle/meat group, the cubes will be transferred to a weighing boat until the target weight is approached. The last cube to be added will be trimmed until the target weight is achieved as close as possible.

J. The actual weights for each muscle/meat group will be recorded in the appropriate field notebook and then transferred into a single chemically clean, 1000-mL I-Chem jar.

K. Deer muscle and liver samples in I-CHEM jars will be immediately placed on ice as described below in section 6.6.

L. Deer heads will be removed using a sawzall. (Absorbent pads and protective sheeting and clothing, including masks and/ or goggles, will be worn during deer head removals.) The deer head (with sample tag attached) will be placed in a plastic bag. Heads will be sent to MDNR for aging and screening for bovine tuberculosis and chronic wasting syndrome after the study is completed.

M. The remainder of each carcass will be placed in a plastic bag and stored frozen until the end of the study.

N. Mops and bleach solution will be used to clean dressing areas following daily activities.

6.6 Sample Preservation and Transport

A secure freezer trailer unit will be used for temporary storage of deer carcasses at the field dressing location. Long term storage of deer carcasses (until study termination) will take place at an off-site storage location yet to be determined. Tissue samples (in I-CHEM jars) will be immediately placed in ice-filled coolers and be transported to the University Research and Containment Facility (URCF) at Michigan State University where they will be stored at –20°C until homogenization. All samples will be continuously tracked, in the field and in transit to the laboratory, by use of the chain-of-custody procedures specified in SOP 401 (Sample Management - Receiving, Preservation, Storage, Documentation, Decontamination, and Disposal).

6.7 Laboratory Sample Preparation

A. Tissue samples will be stored at –20°C until they are ready for homogenization.

B. Tissues will be homogenized in stainless steel blenders. In between samples, blenders will be washed with Liquinox soap, rinsed 3 times with nanopure water, and reagent grade acetone and hexane rinsed.

C. Homogenates will be aliquoted into six separate chemically clean I-CHEM jars. One jar will be shipped to each analytical laboratory, while any remaining jars will be archived at the URCF. Sample IDs will be labeled for each replicate homogenate sample as described in SOP 214 (Documentation, Preservation, Handling, and Tracking of Samples for Analysis).

D. All tissue homogenates will be stored in the -20° C freezer until time of shipment to the analytical laboratory.

E. All laboratory practices will be recorded in the appropriate laboratory notebook.

6.8 Sample Shipping to Analytical Laboratory

Tissue homogenates will be packaged and shipped for analysis according to EPA/REAC guidelines (EPA, 1994). Samples will be shipped in coolers on ice. To prevent leakage during shipping, sample containers will be no more than 90 percent full. The labeled sample containers properly sealed and with the exteriors wiped clean and dry, will be placed in a polyethylene bag. The samples will then be placed in an U.S. Department of Transportation (DOT) approved cooler that has been lined with a large polyethylene bag or plastic sheeting. Because there will be multiple containers per cooler, there will be sufficient cushioning material between them to prevent breakage if the cooler is dropped or severely shocked. One chain-of-custody form will be placed in a watertight bag and taped to the inside of the lid of each cooler. Cooler and box lids will be affixed before shipment, and all containers will be sealed with tape. Coolers will be sealed with signed custody seals prior to shipment.

7.0 RECORDS, DOCUMENTATION, AND QC REQUIREMENTS

This section describes records, documentation, and QC requirements, as applicable.

7.1 Sampling Documentation

For each individual deer that is collected, the following observations and measurements will be recorded at a minimum:

- species
- date collected
- site location and GPS coordinates
- sex

- type of all tissues collected (e.g. liver, rumproast, tenderloin, backstrap)
- weight of all tissue collected
- collectors initials

During mobilization, sample labels will be pre-printed with the project name and a unique sample identification number. Just prior to being secured to the sample container in the field, the following information will be added to the label: (a) data and time of collection; (b) temperature and weather conditions; (c) location; and (d) personnel initials. If the number of containers for a sample set exceeds the number of preprinted labels, blank labels will be used for the additional containers with the sample identification number inserted. The QA/QC samples will be labeled accordingly. Detailed procedures for sample labeling is addressed in SOP 214 (Documentation, Preservation, Handling, and Tracking of Samples for Analysis).

7.2 Quality Assurance

Field blanks and field duplicates will be used to monitor for sampling errors, interferences, and/or contamination that might occur as a result of field sample collection, packaging, or shipping. A field blank will consist of clean sodium sulfate that is prepared, stored, and analyzed for PHAH congeners as if it were an actual sample. This meets EPA's stipulation that field blanks should be submitted at a rate of five percent of the total number of samples. Additionally, two other biota samples will be needed to perform matrix spike/matrix spike duplicate (MS/MSD) analyses. The matrix spikes for deer samples will consist of both liver and muscle homogenates spiked with known concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and 2,3,7,8-tetrachlorodibenzofuran. Matrix spikes will also include PCBs when appropriate for the intended analysis.

7.3 Data Evaluation

Once results of the laboratory analyses have been completed, the average concentrations of PHAH congeners across sampling locations will be calculated. This process, and the subsequent data evaluation, is detailed in the following sections on data compilation, statistical analyses of the results and documentation of the procedure and results.

7.4 Data Compilation

The initial step in data evaluation will be to review the laboratory reports and data sheets for completeness and qualifiers. All of the sampling information will be compiled in a spreadsheet. The following information will be included: sampling ID number, sampling location, date and time of sample collection, lipid content of tissues, and PHAH congener concentrations of tissues. The accuracy of the above data entry will be verified by a scientist other than the one that entered the data. The results of the QA/QC samples (field blanks MS, MSD) will be considered to detect possible sources of interference or contamination.

7.5 Statistical Analysis

The objectives of statistical analysis are to: (a) identify and report the PHAH congener concentrations measured in white-tailed deer that have been collected from the study area; (b) calculate summary statistics; (c) evaluate differences in total PHAH concentrations between study and reference sites; and (d) calculate the potential risk of PHAH exposure to humans.

As an initial step in the statistical analysis of white-tailed deer analytical results, summary statistics will include the range, mean, 95 percent confidence limits on the arithmetic mean, median, geometric mean, standard deviation, and standard error. One-half of the detection limit will be substituted for any non-detect concentrations.

7.6 Schedule

Deer sampling will begin mid-November of 2003 and end by late November 2003. Deer processing as well as tissue collection and homogenization will take place throughout the months of November and possibly December. PHAH analyses will initiate as soon as possible and it is expected that data will be summarized by March 2004.

8.0 RESPONSIBILITIES

Project responsibilities are listed below.

Project Manager —Will oversee and approve all project activities; review QA reports; approve final project QA needs; authorize necessary actions and adjustments to accomplish program QA objectives; and act as liaison between agencies and field staff.

Quality Assurance (QA) Manager —Will oversee all QA activities to ensure compliance with contract specifications; initiate audits on work completed by project personnel and subcontractors, including analytical laboratories and independent data validation contractors; review program QA activities, quality problems, and quality-related requests. In response to field and analytical findings, he will approve the corrective actions. He will report quality non-conformances to the Project Manager and review all pertinent portions of the deliverables before they are transmitted to ensure conformance with QA/QC procedures and quality work product.

Data Manager —Will oversee data management for this project. He is responsible for the structure, organization, format, implementation, and operation of the project database.

Field Team Leader — Will oversee field activities and supervise the field crews. He will ensure that proper sample collection, preservation, storage, transport, and COC QC procedures are followed. He will inform the Project QA Manager when field problems occur, and will communicate and document corrective actions taken. The Field Team Leader will discuss field activities with the Project Manager.

Laboratory Project Manager — The laboratory project manager for this project. He is responsible for assuring that the analysis of all samples is performed in accordance with the QAPP and the laboratory's quality assurance manual. In addition, the Laboratory Project Manager performs the final laboratory review of project data packages for completeness and compliance with project requirements.

9.0 REFERENCES

EPA. (1994). Standard Operating Procedures 2004; Sample Packaging and Shipment - EPA/REAC. U.S. Environmental Protection Agency, Washington, DC. U.S. EPA Contract 68-C4-0022. August 11.

STANDARD OPERATING PROCEDURE

Sample Management: Receiving, Preservation, Storage, Documentation, Decontamination, and Disposal

Version 2 August 6, 2003

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Authored By: Denise Kay, Ph.D., Katherine K. Coady, Ph.D., and Alan Blankenship, Ph.D. Date: 08/06/03

Supervisor Review By: ______________________________ Date: ____________

Reviewed By: ______________________________ Date: ____________
(QA Coordinator)

DEFINITIONS AND ACRONYMS

CAR	Corrective Action Report
COC	Chain of Custody
CQA	Chemical Quality Assurance
LIMS	Laboratory Information Management System
PPE	Personal Protective Equipment
QA	Quality Assurance
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure
SOW	Scope of Work
STS	Sample Tracking Sheet
USFWS	United States Fish and Wildlife Service
MDNR	Michigan Department of Natural Resources

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1.0 PURPOSE

This standard operating procedure (SOP) specifies the requirements for sample receipt, control, record keeping, decontamination, and disposal at the ENTRIX, Inc.

2.0 SCOPE AND APPLICATION

This SOP applies to samples collected by ENTRIX personnel from field studies.

3.0 SAFETY CONSIDERATIONS

Safety training and medical monitoring requirements are described in the Health and Safety Plan for the appropriate field studies.

In addition, there are various safety concerns regarding the receipt, storage, and disposal of sample containers. Upon receipt, the sample containers will be monitored for breakage. If sample containers are broken, the appropriate personnel will be immediately notified.

3.1 Personal Protective Equipment

Personnel protective equipment (PPE), consisting of lab coats, safety glasses, and latex gloves will be worn at all times when handling samples.

3.2 Waste Management

All waste will be managed and disposed in accordance with applicable local, state, and federal regulations. Waste management practices will include the control of all standards and solutions. This means that expired or used standards and associated solvents will be disposed of in labeled waste containers and the appropriate personnel will be notified for waste pick up.

3.3 Sample Decontamination

If a spill occurs in the laboratory, the appropriate personnel will be notified immediately. The area where the spill occurred will be evacuated and marked. The appropriate personnel will then clean the spill area.

4.0 EQUIPMENT, MATERIALS, AND REAGENTS

The sample storage area is equipped with a personal computer, which is used to log samples and a locked freezer, in which samples are stored. The freezer contains a calibrated thermometer that is used to check temperature daily. A calibrated balance is also kept in the sample storage area and is used to weigh sub-samples.

No materials or reagents are used in sample receipt.

5.0 METHOD, PROCEDURES, AND REQUIREMENTS

5.1 Sample Receipt

The physical condition of coolers or other containers used for transportation, and each individual sample containers will be inspected upon arrival at the laboratory. The following objectives are established for sample receiving:

A. Inspect sample coolers and samples for signs of damage upon receipt at the laboratory.

B. Attach air bill or shipping receipt to the chain of custody (COC) form.

C. Examine individual samples and record their status (frozen/ not frozen) on a sample receipt form.

D. Verify that a COC form is submitted with samples, and that the COC contains all information required for analysis and reporting. Maintain custody of samples by ensuring that all dates, times, and signatures are provided on the COC forms.

E. Identify and reconcile any discrepancies between the COC and sample labels.

F. Verify that sample container labeling, or other requirements are correct. Assign a unique lab identification number to each sample and log samples into the sample-tracking sheet (STS). (See attached STS.) Identify any hazards or special precautions associated with the incoming samples.

G. Notify appropriate laboratory and field study personnel when samples have arrived. These individuals are to be identified in either a Work Plan or SAP.

H. Track and document the handling of samples from receipt through data reporting to final disposal. This will be accomplished by keeping all log forms in a laboratory binder.

5.2 Sample Documentation

Upon arrival, the shipping receipts will be collected from the cooler and be stapled to the COC form. Samples submitted to the laboratory will be accounted for by documenting their arrival and condition on COC and sample tracking sheets. Within the laboratory, the STS will be used to monitor the samples whereabouts at all times. Aliquots removed will be recorded on the STS. While handling samples, any anomalies or problems will be noted in bound laboratory notebooks that are kept in the same binder with the STS.

5.3 Sample Storage and Preservation

Samples will be stored in a freezer in the laboratory. This room is accessible only to lab personnel. The freezer will be set at -20° C, and the temperature will be monitored daily and be documented on a freezer log sheet. If for any reason there is a power outage, the facility manager on call will be immediately notified by beeper. The necessary action will then be taken to ensure that sample integrity is not compromised. If samples are removed from the freezer for any reason, this activity will be documented on the STS and COC form. Copies of the forms will be placed in the records archive. When samples are removed for preparation and analysis, a sample extraction form will be completed.

5.3.1 Scheduled Monitoring

All refrigerators and freezers used in the laboratory will be examined frequently due to constant use. Freezer temperatures are maintained at a nominal -20° C. If the temperature rises to -15° C, corrective action must be taken. Actions include adjusting the thermostats, having the unit serviced, or moving the samples to another unit.

5.3.2 Sample Accountability

To ensure that all samples will be accounted for, the following guidelines will be followed:

A. The person obtaining the sample or submitting the sample to the laboratory for analysis must establish sample identity.

B. Integrity of sample must be maintained from collection to delivery.

C. Composition of sample must remain the same during handling and storage before analysis.

D. Evidence must exist of sample’s receipt, and the COC record will be filled out and appropriate personnel notified of the sample arrival.

E. Person preparing the samples must not allow composition of samples to change or integrity to be questioned.

F. Analyst must ensure correct sample is analyzed.

G. Analyst must record all data contributing to the analysis.

H. Records must be kept to trace sample from retrieval through data reporting.

I. Special storage conditions must be documented.

5.3.3 Label and COC Discrepancies

Discrepancies between the sample labels and COC will be noted on the COC or Sample Receipt Form. The sample manager will resolve any documentation discrepancies by contacting personnel that submitted samples. For discrepancies impacting sample viability (i.e., improper sample temperature) where a CAR is required to be completed, the sample manager will coordinate with the sample submitter, QA, and Project Study Group representatives to determine the appropriate corrective action.

6.0 RECORDS, DOCUMENTATION, AND QC REQUIREMENTS

The primary analyst shall document any anomalies and/or deviation from the specified method in a bound, serially numbered, laboratory notebook with tear-out carbon copies. All electronic files and hardcopies will be kept at the participating laboratory.

The carbon copies from data notebooks will be removed and archived in a separate building. Copies of the COC forms, the STS, and laboratory notes will be kept in 3-ring binders in separate places at all times in case of fire or other disaster.

7.0 RESPONSIBILITIES

Project responsibilities are listed below.

Project Manager —Will oversee and approve all project activities; review QA reports; approve final project QA needs; authorize necessary actions and adjustments to accomplish program QA objectives; and act as liaison between agencies and field staff.

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8.0 REFERENCES

Comprehensive Analytical Laboratory Services Quality Assurance Management Plan, April 1997.

Environmental Analytical Laboratory, Laboratory Quality Control Plan, April 1997.

STANDARD OPERATING PROCEDURE

Maintenance of Sample Integrity, and Proper Usage of Refrigerators, Freezers, and Liquid Nitrogen Dewars

Version 2 August 6, 2003

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Supervisor Review By: ______________________________ Date: ____________

Reviewed By: ______________________________ Date: ____________
(QA Coordinator)

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1.0 PURPOSE

Guidelines have been established to ensure that refrigerators and freezers are used in a safe, clean, and efficient manner.

2.0 SCOPE AND APPLICATION

The following procedure outlines proper usage of refrigerators and freezers by the members of the laboratory, as well as sample logging and treating procedures.

This procedure describes guidelines for safe storage of samples and standards, sample storage locations, restrictions on the types of materials that may be stored in certain units, sample access, temperature monitoring, protection of sample integrity and alarm systems.

3.0 SAFETY CONSIDERATIONS

Safety training and medical monitoring requirements are consistent among all protocols, and are described in the Health and Safety Plan for each research project.

4.0 METHOD, PROCEDURES, AND REQUIREMENTS

4.1 Sample Storage Locations

A. Water and sediment samples are sometimes kept in short-term storage (24 to 48 hours) in a walk-in cooler.

B. A walk-in freezer is also used to store tissue samples and carcasses from field and laboratory studies. The walk-in freezer is maintained at -20° C and the walk-in cooler is maintained at 4° C.

4.2 Sample Access

The laboratory facility is locked at all times and is considered very secure. Each employee authorized to work there has a key to enter the building. The walk-in freezer and cooler are locked and access to these rooms is limited to laboratory personnel.

4.3 Scheduled Monitoring

All refrigerators and freezers are examined frequently due to constant use and monitored weekly by reading the temperature from a thermometer located in each unit and recording the temperature in the Maintenance Log for Refrigerators, Freezers, and LN Dewars. Freezer temperatures are maintained at -20° C. If the temperature rises to -15° C, corrective action must be taken. Corrective actions include adjusting the thermostat, having the unit serviced, and/or moving the samples to another unit. Any incidents requiring corrective action are recorded in the Maintenance Log.

4.4 Alarm System

The walk-in freezer and walk-in cooler can tolerate brief power outages or malfunctions without compromise of the samples they contain because of their large volume and large stored mass. However, it is important that any such malfunctions or power outages are recognized promptly; therefore, the walk-in freezer and walk-in cooler are protected by temperature alarm systems. Instructions for these systems are posted under the alarm bell in the hallway and are reproduced below. When the alarm sounds, the freezers are all connected to the emergency generator. Be sure that the cause of the power outage is identified and corrected.

FREEZER ALARM

If the above alarm is ringing, it means that this freezer / refrigeration unit has a serious problem. Please take one of the actions listed below to save valuable research materials.

1. Consult the Laboratory On-Call List posted on the wall by the nearest telephone and call the responsible person.

2. Report electrical and freezer malfunctions to the laboratory building manager, whose office is located just inside the main front doors.

Any personnel who responds to an alarm will visually inspect the unit that gave the alarm and comment in the Maintenance Log binder. An estimate of the amount of time the unit was not functioning properly should be entered under Comments. If there is not enough space on the log sheet for a thorough description of the incident, refer the reader to the Additional Notes section and place a full report there. All electrical and freezer malfunctions should be reported to the laboratory building manager.

The walk-in freezer and walk-in cooler are connected to an audible alarm and an auxiliary generator. If power from the main power grid is lost, the auxiliary generator automatically provides power and an alarm is called to "on call" laboratory personnel. There are two individuals on call at all times. These individuals can be contacted by telephone and carry pagers at all times.

4.5 Guidelines for Proper use of Refrigerators / Freezers

A. All samples, standards, and reagents should be properly labeled with the identification of the substance in the container and the date. If appropriate, hazard warnings, concentration, and an expiration date should be added. All incoming chemicals should be labeled with the full name of the receiver and the date of receipt and should be logged into either a logbook or a database. Note: It is not acceptable to label only the rack holding many small tubes or vials.

B. Sample labels: All stored samples should be given new labels within 13 months past the date on the label. All samples must be in labeled sample boxes with a closing lid. Each individual sample in the box should be labeled with the following:

Project name:
Date collected:
Date placed in freezer/ cooler:
Sample type: (e.g. rainbow trout carcass)
Client name:
Client's sample ID:
Sample tracking # (Chain of Custody):

Samples should be labeled on the outside of the container or package. Use only permanent, waterproof markers to write on glass or plastic.

C. Sample Box Labels: Samples should be grouped by project and/or sample type and placed in the storage boxes. Boxes should be labeled with the following information:

Project name:
Sample type:
Date placed in freezer:
Name of person who collected sample:
Client Name:
Location where sample was collected:
List of sample #s in box:

A sample log sheet should be filled out and a copy placed in both the sample box and the sample log binder. When a sample box is logged, the number corresponding to the area where it is stored should be recorded on the appropriate line in the logbook. This system makes the task of finding a sample box much simpler and minimizes the amount of time that the deep freeze door is open. An entry should be made in the Maintenance Log every time the freezer is entered so that in case of a malfunction, it can be determined when the unit was last known to be functioning properly.

D. Samples and analytical standards should be kept in separate refrigerators or freezers.

E. Food or beverages for human consumption should never be stored in a refrigerator or freezer where standards, samples, or reagents are stored.

F. Buffers such as TRIS, HEPES, and phosphate buffers should be kept for no longer than one month. The pH of a buffer should be checked regularly at the temperature at which the buffer is intended to function. Buffers with sucrose should be filtered before storage; filtering will increase the storage life to no longer than two weeks. Buffers should be marked with an expiration date and disposed of after that date.

G. Samples and standards should be kept in containers that will prevent them from spilling or otherwise contaminating other stored materials. Items easily tipped or without tight lids should be placed inside other containers to prevent spilling. For example, a flask with a Parafilm cover might be placed inside a wide beaker.

H. Each person using storage space in a refrigerator or freezer should check routinely (once a month) for old buffers, glassware, etc., that he/she has left behind and should remove unneeded items.

I. For reasons of cleanliness, safety, and limited space, each person using storage space in a refrigerator or freezer may remove any items not in compliance with the above guidelines to a designated area in another refrigerator or freezer. Every reasonable effort must then be made to contact the person responsible, including contact by mail and telephone, and a note describing the item(s) removed and the new storage location should be posted on the refrigerator or freezer in which the items were found. If the items are not claimed and dealt with properly, they will be destroyed one month after removal.

4.6 Safety and Usage of Liquid Nitrogen Dewars

(Taken from the CRC Handbook of Laboratory Safety)

A. Flammability: Liquid nitrogen, liquid helium, and metal surfaces made very cold by liquefied gases can condense oxygen from the atmosphere, causing oxygen to build up or become entrapped in enclosed spaces. This greatly increases the risk of fire, and may cause even non-combustible materials like carbon steel to burn under the right conditions. Make sure that the area where liquid nitrogen Dewars are stored is well ventilated.

B. High Pressure: Liquefied nitrogen is stored at or near its boiling point, so that some gas is always present in the container that holds it. Be aware that liquid nitrogen expands rapidly when allowed to warm up, so make certain that containers that hold it include an allowance for the gaseous phase.

C. Materials: Materials that are otherwise pliable or tough may become brittle and shatter under the extreme cold temperatures of liquid nitrogen. Materials suitable for cryogenic temperatures include Dacron, Teflon, Kel-F, asbestos impregnated with Teflon, Mylar, Nylon, stainless steel (300 series), copper, bronze, aluminum, and brass. Important: Do not use glass vials to store samples in a liquid nitrogen Dewar. The glass will shatter. Use only plastic Cryovials with tamper-proof vinyl stick-on labels. Also, do not use wooden materials with liquid nitrogen, since wood (or asphalt) saturated with oxygen might explode when subjected to mechanical shock. If in doubt, consult a materials manual or call ORCBS to make certain that liquid nitrogen will not cause a problem with the materials with which it is to be used.

D. Personnel:

1. Avoid hazards of fire, high pressure, and material failures listed above.

2. Even very brief contact of body parts with fluids or materials at cryogenic temperatures can cause burns similar to thermal burns. Prolonged contact will cause exposed parts to freeze and become brittle. The eyes are particularly sensitive to this type of trauma, so always wear eye protection while working with liquid nitrogen.

3. While liquid nitrogen is not itself toxic, it can cause asphyxiation by displacing air, so store and use liquid nitrogen only in well-ventilated areas.

4. Equipment should be kept very clean to avoid dangerous contamination of liquid nitrogen stores.

5. When there is a possibility of personal contact with liquid nitrogen, wear full-face protection, an impervious apron or lab coat, cuffless trousers, and closed shoes (no sandals). Do not wear jewelry. Gloves may or may not be worn. If worn, gloves should be impervious and loose fitting so that they can be easily thrown off the hand if liquid nitrogen is spilled inside them. Potholder type protection for the hands is probably best. Do not touch the interior of the Dewar or anything that has been recently removed from it without protection for the hands.

6. Do not tilt a Dewar flask to pour out the liquid, as this may damage the container.

E. Contamination: Oxygen can build up in liquid nitrogen containers if the cap is not kept on or if the entire volume of liquid in the container is not occasionally replaced, i.e., the Dewar is continually refilled from larger containers without ever allowing it to become totally empty, increasing the chances of contamination with oxygen. If the liquid takes on a bluish color, it is contaminated with oxygen and should be treated as a dangerous, potentially explosive material.

5.0 RESPONSIBILTIES

Project responsibilities are listed below.

Project Director: Dr. Alan Blankenship —Will oversee and approve all project activities.

Project Manager: Dr. Denise Kay — Will oversee and approve all project activities; review QA reports; approve final project QA needs; authorize necessary actions and adjustments to accomplish program QA objectives; and act as liaison between agencies, field staff.

Quality Assurance (QA) Manager: Dr. Paul Jones — Will oversee all QA activities to ensure compliance with contract specifications; initiate audits on work completed by project personnel and subcontractors, including analytical laboratories and independent data validation contractors; review program QA activities, quality problems, and quality-related requests. In response to field and analytical findings, he will approve the corrective actions. He will report quality non-conformances to the Project Manager and review all pertinent portions of the deliverables before they are transmitted to ensure conformance with QA/QC procedures and quality work product.

Data Manager: Dr. Denise Kay — Will oversee data management for this project. He is responsible for the structure, organization, format, implementation, and operation of the project database.

Field Team Leader: Mr. Patrick Bradley — Will oversee field activities and supervise the field crews. He will ensure that proper sample collection, preservation, storage, transport, and COC QC procedures are followed. He will inform the Project QA Manager when field problems occur, and will communicate and document corrective actions taken. The Field Team Leader will discuss field activities with the Project Manager.

Laboratory Project Manager — The laboratory project manager for this project. He is responsible for assuring that the analysis of all samples is performed in accordance with the QAPP and the laboratory's quality assurance manual. In addition, the Laboratory Project Manager performs the final laboratory review of project data packages for completeness and compliance with project requirements.

6.0 REFERENCES

Good Laboratory Practice Standards. 40 CFR Part 160. Environmental Protection Agency, 1989.

Steere, Norman V. CRC Handbook of Laboratory Safety. Chemical Rubber Co., Cleveland, 1967. pp 314-323.

STANDARD OPERATING PROCEDURE

Data Package Review

Version 2 August 6, 2003

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Reviewed By: (QA Coordinator)	________________________________	Date: _____________

DEFINITIONS AND ACRONYMS

CCV	Continuing Calibration Verification
COC	Chain of Custody
CQAP	Chemical Quality Assurance Plan
DOC	Dissolved Organic Carbon
EAL	Environmental Analytical Laboratory
EDD	Electronic Data Deliverable
GC/MS	Gas Chromatography/Mass Spectrometry
ICV	Initial Calibration Verification
IDs	Identifications
GC	Gas Chromatograph
LCS	Laboratory Control Sample
LIMS	Laboratory Information Management System
QA	Quality Assurance
QAC	Quality Assurance Coordinator
QC	Quality Control
SOP	Standard Operating Procedure
TOC	Total Organic Carbon

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1.0 PURPOSE

The purpose for data package review is to ensure that final results reported are an accurate representation of the raw data generated during analysis. Data packages must function as stand-alone units. They must contain all information necessary to verify the reported results and to completely document the quality control procedures utilized during the analysis. Any deviations from the written protocol and/or quality control procedures, which do not meet the documented limits, must be clearly noted in the data package.

2.0 SCOPE AND APPLICATION

Data package review is applicable to all data packages generated by ENTRIX in conjunction with a project work plan. Two levels of review will be performed on each data package prior to submission of the data package to the Quality Assurance Coordinator. The first level of review will be performed by the primary analyst (analyst who performed the analysis or his/her designee). The second level of review is to be performed by the lead supervisor or their designee. Both levels of data package review must be documented utilizing the appropriate checklist (See Attachments 1 and 2). A Quality Control (QC) review will be performed at a frequency of 20% of samples. The QC review will be performed as detailed on the QC Lot Folder Review Checklist (Attachment 3).

3.0 SAFETY CONSIDERATIONS

All personnel shall adhere to prudent safety practices as specified in the project Health and Safety Plan (HASP).

4.0 EQUIPMENT, MATERIALS, AND REAGENTS

The data package reviewers will require basic office equipment including, at a minimum, pens, a calculator and a computer. The computer must be loaded with Reflections for access to the LIMS software and should have the ability to review raw analytical data when required.

5.0 METHOD, PROCEDURES, AND REQUIREMENTS

Three levels of data review will routinely be performed:

Analyst Review

Technical Review

Quality Assurance Review

5.1 Primary Analyst Review

A. Once the data package has been generated, in accordance with ENTRIX SOPs, the analyst, or their designee, will perform the first level of review. This review will verify the completeness of the data package prior to submission for technical review.

B. Review the Lot Folder Tracking Form. Verify that the header information is correct. Verify that the collection and analysis dates for samples are correct.

C. Each package will contain a data package checklist, appropriate for the method performed (See Attachments 3 and 4 for examples). Verify that the data package includes all required forms as listed on the appropriate data package checklist. Verify that the data package is assembled in the order detailed on the appropriate data package checklist. Verify that the review of the contents have been performed by checking off each specific item on the appropriate data package checklist.

D. The primary analyst must verify each item on the appropriate Review Checklist. The review of each item must be noted by checking the appropriate item on the checklist.

E. Review the LIMS Work list printout and the client and internal Chains-of-Custody (COCs). Verify that all samples on the client and internal COCs match the samples on the work list and that there are no transcription errors or omissions.

F. Verify that there are no transcription errors on the LIMS work list printout by checking the results against the raw data.

G. Check all QC sample results. Ensure that all quality control samples met acceptance criteria specified in the appropriate method SOP. If any QC samples do not meet criteria, verify that this is noted in the Case Narrative and also in the Analyst Comments section of the data package checklist. Verify that there is sufficient explanation regarding data acceptability.

H. Verify that all unused lines and entries on all forms have been lined out, dated, and initialed.

I. Verify that the correct calibration standards were used for quantitation.

J. Verify that all-raw data for the analyses are included.

K. Verify correct calculation of results by recalculating the reported result on the Example Calculation Form.

L. Verify that all pages in the data package, that require analyst signatures, have been signed and dated by the analyst.

M. Document all variations from the SOP or problems with the analytical run in the Case Narrative (Refer to SOP 216, Data Package Generation).

N. If applicable, verify that the data package is consecutively paginated and that an EDD has been generated.

5.2 Technical Review

A. The technical review is the second level review and is performed by the Lead Supervisor or their designee. The technical review is performed to confirm the completeness of the package as submitted by the analyst and to verify the technical validity of the reported results.

B. Review the Lot Folder Tracking Form. Verify that all header information is included and is accurate. Review the items listed in the Case Narrative Form and add pertinent information, as appropriate. Sign and date the Lot Folder Tracking Form for Technical Review.

C. Each package will contain a data package checklist that is appropriate for the method performed (See attachment 4 for an example). Verify that the data package includes all required forms as listed on the data package checklist. Verify that the data package is assembled in the order detailed on the appropriate data package checklist. Verify that the primary analyst has checked off all applicable items on the appropriate data package checklist.

D. Each data package will contain the appropriate Method Review Checklists. Verify that the primary analyst has completely and correctly filled out the Review Checklists. Verify that the primary analyst has signed and dated the checklist. Verify that items listed on the form have been included in the data package and that all information is accurate. Sign and date the Review Checklists as the Reviewer.

E. Review the LIMS work list printout. Verify that there were no transcription errors for the reported results by reviewing the raw data. Verify that all QC sample recoveries are reported correctly. Sign and date the LIMS report as the Reviewer.

F. Review the Internal Chain-of-Custody to ensure that custody was maintained within the laboratory. Signatures and dates must be present for all exchanges of samples between personnel. Verify that all client COCs are included for all samples contained on the Internal COC.

G. Review the Sample Preparation Form, if applicable. This form must include preparation information for all samples present in the analytical run(s). Verify that the following has been completed: all header information, sample IDs, sample initial and final weights or volumes, units, solvent used with manufacturer's name and lot number, spike volumes and solution IDs. Ensure that sample preparation steps and holding time requirements have been met. Verify that the spiking solutions are traceable to certified reference materials and the traceability has been clearly documented in the data package. Verify that none of the stock or working standards used for spiking have expired. Verify that the source used for the LCS is different from the source used for the initial calibration standards. The source for the Matrix Spike (MS) may be from the same source as the LCS or the initial calibration standards. All unused lines must be crossed out, initialed, and dated.

H. Review the Additional Sample Preparation Information Form, if applicable. The steps involved in the preparation process must be clearly defined with all initial and final volumes clearly stated. All unused lines must be crossed out, dated and initialed.

I. Review the Sample Preparation Comments Form, if applicable. Verify that the header information is complete and accurate. Verify that the analyst included any comments regarding the sample preparation process which may affect the results and which deviate from the specified method. If there were no reportable instances affecting the data, verify that the analyst indicates this. All unused lines must be crossed out, dated and initialed by the analyst.

J. Review the Sample Extract Dilution Form, if applicable. Verify that the header information is complete and accurate. Verify that the Sample IDs and extract and solvent volumes and units are correct. Verify that the resulting dilution factors are correctly calculated. All unused lines must be crossed out, dated and initialed by the analyst.

K. Review the Solvent Purity Form, if applicable. Verify that the header information is complete and accurate. Verify that any solvents used for the method have had the solvent purity verified. As laboratory de-ionized water is continuously monitored, documentation using this form is not required.

L. Verify the calibration of the instrument. Documentation of the calibration may consist of the Calibration Form, GC/MS tune reports and calibration reports, or the use of a spreadsheet or other documentation specified in the method SOP. Raw responses must be checked for accurate data transcription and acceptable calibration results. Verify that all calibration information presented on the raw data has been accurately transcribed onto the calibration forms. Verify that all instrument calibration criteria (initial calibration verification (ICV), continuing calibration verification (CCV), instrument drift checks, etc.) meet the requirements detailed in the LQCP and/or method SOP. For daily calibration checks, verify that the daily standard is checked against the correct initial calibration. Any manual integration of calibration standards require clear identification, a hardcopy of the ‘before’ and 'after' chromatograms for the manual integration, and an explanation for the use of manual integration.

M. Verify that all calibration and QC standard sources meet the requirements of the LQCP and associated method SOP. Verify that the calibration solutions are traceable to certified reference materials and the traceability has been clearly documented in the data package.

N. Verify that all associated raw data are included in the data package. Review the responses for all sample and QC analyses. Raw responses must be checked for accurate data transcription, if applicable. If a spreadsheet is used for interpretation of raw data, check for accurate data transcription. Confirm analysis holding time is within requirements. Verify that final concentrations have been calculated correctly by checking 10% of reported results. Check raw data for obvious problems, this may include elevated baselines, peak tailing, retention-time shifts, interfering ions, etc.

O. Verify that the analysis was in control by evaluating the recoveries observed for the QC samples. The method blank result should be below the method specific limits (MDL, PQL, MRL, etc). If there are concentrations present in the method blank at levels above the method specific limits, then professional judgement must be used to determine if the data are acceptable. This must be noted on the Case Narrative.

P. Verify that a matrix spike was performed and is included in the Data Package. Verify that the matrix spike recoveries are acceptable.

Q. Verify that all standards used for the sample preparation and analysis have not expired. Verify that all required stock and working standards logbook pages are included. Verify that all standards can be traced back to a certified standard reference material and that all Certificates of Analysis are included.

R. Verify that the report is consecutively paginated and that the EDD has been generated. If the report is not paginated and/or the EDD is not generated, perform these functions.

S. Although each data package is a stand-alone entity assessment of results particularly for laboratory control samples and certified reference materials should be compared to those of preceding data packages to detect possible trending of data with time. Should any trending be detected the data in all packages should be examined closely to determine the cause of any trends observed.

5.3 Quality Control (QC) Review

A. A QC review will be performed at a frequency of 20% of samples. The QC review will be performed utilizing the QC Lot Folder Review Checklist. For each portion of the data package to be reviewed, check each item listed on the QC Lot Folder Review Form to ensure completeness and accuracy.

B. If QC or technical discrepancies are identified in the 20% data package review, the QC reviewer should use their professional judgement in determining whether more than 20% of the data packages should be reviewed.

C. Verify that anomalies, variations, or problems are stated in the Case Narrative Section.

D. Verify that all necessary forms are included in the data package.

E. Verify that the field COC, Lab COC, LIMS work list and Chain-of-Custody information is complete and accurate.

F. Verify that all sample preparation information is complete and accurate, and that sample prep and analytical holding time requirements have been met.

G. Verify that the calibration information is complete and accurate.

H. Verify that the sample response information is complete and accurate.

I. Verify that method blank, laboratory control spike, and matrix spike samples were performed and accurately reported. Verify that the QC samples meet the method specific criteria.

J. Sample integrity and traceability will be assessed in 2 samples per data package by performing a full audit trail analysis. The audit trail will track the sample documentation from field collection through final reporting and will include verification of sample documentation, sample container labeling and all COC and analytical procedures.

K. Sign and date the QC Review Checklist.

L. Upon completion of the QC review, any discrepancies in the data package should be brought to the attention of the Lead Supervisor for resolution.

6.0 RECORDS, DOCUMENTATION, AND QC REQUIREMENTS

A. The primary analyst shall document any anomalies and/or deviations from the specified method in the appropriate sections of the data package and list them in the Case Narrative Form. The primary analyst will sign and date any forms as the analyst.

B. The technical reviewer will record any problems noted during the technical review. The technical reviewer will return the data package to the analyst for corrections prior to submission of the data package. The technical reviewer must sign and date all forms as the reviewer.

C. The technical reviewer, or their designee, will paginate the report.

D. Generation of EDDs will be performed by the technical reviewer or by a designee of the technical reviewer or lead supervisor. As the nature of the EDD will vary considerably for each sample type and analytical procedure it is not possible to provide a definitive description of specific EDDs. EDDs will take the format of summary tables that may be directly extracted from the data package but may also consist of scanned documents in electronic format suitable for electronic storage, transmission and retrieval. QC procedures for summary tables will be determined based on the method of generation. EDDs will be provided in a format that will allow them to be suitably protected from electronic manipulation of the data.

E. The QC reviewer will document any findings on the QC Lot Folder Review Checklist and notify the Lead Supervisor(s) and primary analyst.

7.0 RESPONSIBILITIES

Project responsibilities are listed below.

Project Director: Dr. Alan Blankenship —Will oversee and approve all project activities.

Project Manager: Dr. Denise Kay — Will oversee and approve all project activities; review QA reports; approve final project QA needs; authorize necessary actions and adjustments to accomplish program QA objectives; and act as liaison between agencies, field staff.

Quality Assurance (QA) Manager: Dr. Paul Jones — Will oversee all QA activities to ensure compliance with contract specifications; initiate audits on work completed by project personnel and subcontractors, including analytical laboratories and independent data validation contractors; review program QA activities, quality problems, and quality-related requests. In response to field and analytical findings, he will approve the corrective actions. He will report quality non-conformances to the Project Manager and review all pertinent portions of the deliverables before they are transmitted to ensure conformance with QA/QC procedures and quality work product.

Data Manager: Dr. Denise Kay — Will oversee data management for this project. He is responsible for the structure, organization, format, implementation, and operation of the project database.

Field Team Leader: Mr. Patrick Bradley — Will oversee field activities and supervise the field crews. He will ensure that proper sample collection, preservation, storage, transport, and COC QC procedures are followed. He will inform the Project QA Manager when field problems occur, and will communicate and document corrective actions taken. The Field Team Leader will discuss field activities with the Project Manager.

Laboratory Project Manager — The laboratory project manager for this project. He is responsible for assuring that the analysis of all samples is performed in accordance with the QAPP and the laboratory's quality assurance manual. In addition, the Laboratory Project Manager performs the final laboratory review of project data packages for completeness and compliance with project requirements.

8.0 REFERENCES

Field and Laboratory Policies and Procedures Manual, 1996, Department of Fisheries and Wildlife, Michigan State University, East Lansing, MI 48824.

Data Quality Objectives Process for Superfund, Office of Emergency and Remedial Response, EPA 540-R-93-071, September 1993, United States Environmental Protection Agency, Washington DC 20460.

Standard Operating Procedure 228, 1996, Aquatic Toxicology Laboratory, Michigan State University, East Lansing, MI 48824.

Quality Assurance Project Plan, April 1997, Aquatic Toxicology Laboratory, Michigan State University, East Lansing, MI 48824.

9.0 ATTACHMENTS

Attachment 1: Extraction Review Checklist

Attachment 2: H4IIE-luc Review Checklist

Attachment 3: QC Lot Folder Review Checklist

Attachment 4: Data Package Checklist

DRAFT

Appendix E. Scientific Collector's Permit

Appendix F. Work Scope for the Wild Game Sampling Interim Response Activity

October 20, 2003

Work Scope for the Interim Response Activity of Evaluating Wild Game Taken from the Tittabawassee River Floodplain

Purpose: This document is provided as an overview (i.e. Work Scope) from which detailed Interim Response Activity (IRA) work plans will be developed for collecting and evaluating concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in wild game taken from the Tittabawassee River floodplain downstream of Midland compared to wild game taken from a reference area located on the floodplain upstream of Midland. The purpose of this study is to determine if wild game taken from the Tittabawassee River floodplain represents a relevant human exposure pathway to PCDDs and PCDFs or not. This document is supplemental to the *Remedial Investigation Scope of Work for Corrective Action Beyond the Facility Boundary Tittabawassee River and Floodplain*, submitted by Dow to Michigan Department of Environmental Quality (MDEQ) on August 11, 2003. Once this Work Scope is approved by MDEQ, Dow will submit for MDEQ approval, the detailed IRA work plan for the wild game sampling, analysis, and evaluation.

Approach: The IRA work plan will describe the approach to obtain ten deer, turkey, and rabbits[1] from each of two locations within the Tittabawassee River floodplain downstream of Midland and ten deer, turkey, and rabbits from a reference location that is located within the floodplain upstream of Midland. Proposed samples will be representative of legally hunted animals and will therefore include both male and female adult deer, turkeys, and rabbits. The IRA work plan will also propose methodology to develop objective criteria to evaluate the need for active exposure control or risk mitigation for the protection of human health and welfare.

The IRA work plan will describe the process by which representative samples of muscle and liver (deer only) that will be taken from each species and analyzed for PCDDs and PCDFs. It will also describe how the results (i.e. concentrations of PCDDs and PCDFs) from samples (i.e. deer, turkey, and rabbit tissue) taken from the reference location will be compared to sample results taken from the two locations within the floodplain downstream of Midland. These comparisons will first be a mathematical comparison of results, to determine if there is a statistically significant increase in concentrations of PCDDs and PCDFs in wild game samples taken from the floodplain downstream of Midland as compared to wild game taken from the reference area. The results will also be compared to concentrations of PCDDs and PCDFs reported in the national food supply and/or other references for the same or similar species (e.g. beef and chicken). All results will be submitted for MDEQ review. Results will include congener-specific PCDD and PCDF data for each sample on a wet weight and lipid-normalized basis, summary statistics, and a comparison of total TEQs and congener patterns. In addition, a sub-sample of deer muscle will be analyzed for PCBs on a congener-specific basis (including coplanar PCBs). The PCB data will be used to determine the relative contribution of PCBs to total TEQs.

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[1] In the event that rabbits are not abundant (due to habitat suitability-related issues), it may be necessary to substitute squirrels in place of rabbits in the IRA work plan.

October 20, 2003

Work Plan:

The IRA work plan will propose methodology to develop objective criteria to determine, based upon the results of the investigations, if further wild game sampling is needed or if active exposure control or risk mitigation is immediately needed to protect human health. The IRA work plan will include:

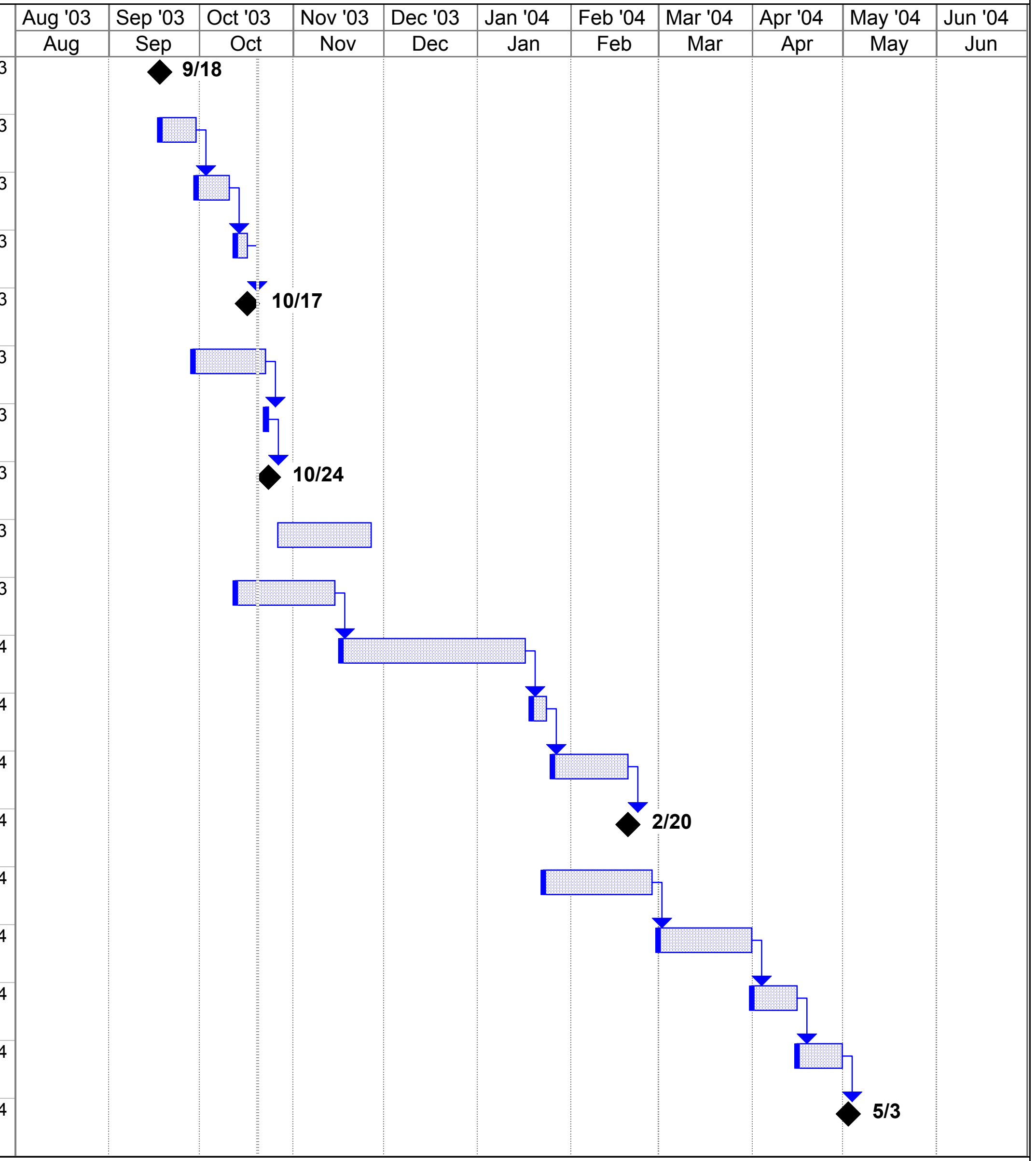
- A description of the specific parcels of property where samples will be taken;
- A physical description of the sampling locations;
- A detailed description of the number and type of samples to be taken, how samples will be processed and analyzed, and how results will be reported;
- A description of existing concentration data for PCDDs and PCDFs from soils in the area where wild game samples are taken and analysis of soils for PCDDs and PCDFs where existing information is not available or is insufficient to characterize the sample locations;
- A description of the comparative statistical tests to be employed for evaluating samples taken within the floodplain to those taken from the reference area (for deer, this may include stratification by sex and perhaps by age if the data allow);
- Proposed methodology to develop criteria for making objective decisions on whether any further data collection and/or analysis is necessary to better understand the situation, including a power analysis based on the observed variability in concentrations within and among locations;
- Proposed methodology to develop criteria for making objective decisions on whether additional Interim Response Activities are needed to mitigate exposure via this pathway; and
- A detailed schedule for implementation of the IRA work plan and submission of the final report for MDEQ review and approval.

In an effort to streamline this process, the IRA work plan will not include formal Project Management Plans, Data Collection Quality Assurance Plans or Data Management Plans. Rather, they will include a Standard Operation Procedure, which will reference existing guidance, e.g., SW-846, or already existing Dow Project Management Plans, Data Collection Quality Assurance Plans and Data Management Plans. Copies of such plans will be provided to MDEQ upon request.

Schedule: The wild game sampling plan and its elements are shown in Figure 1.
In recognition of the need to collect samples during the targeted sampling window (i.e. Fall of 2003) and provide timely information to all interested stakeholders, sampling may begin after Dow receives conceptual approval of the draft detailed IRA work plan (prior to final MDEQ approval of the draft detailed IRA work plan).

Figure 1. The proposed major elements, sequencing, and estimated timeline for the Wild-Game Sampling.

ID	Task Name	Duration	Start	Finish
1	Planning and scoping meeting with MDEQ, MDNR, USFWS	1 day	Thu 9/18/03	Thu 9/18/03
2	Development of Draft Work Scope for Wild Game Sampling (WGS)	8 days	Thu 9/18/03	Mon 9/29/03
3	MDEQ review of Draft Work Scope for WGS	9 days	Tue 9/30/03	Fri 10/10/03
4	Revision of Draft Work Scope for WGS based on MDEQ review	4 days	Mon 10/13/03	Thu 10/16/03
5	MDEQ review and approval of Work Scope for WGS	1 day	Fri 10/17/03	Fri 10/17/03
6	Development of Draft Detailed WGS Interim Remedial Action (IRA) Work Plan	18 days	Mon 9/29/03	Wed 10/22/03
7	MDEQ conceptual review of Draft Detailed WGS IRA Work Plan	1 day	Thu 10/23/03	Thu 10/23/03
8	Obtain MDEQ conceptual approval of Draft Detailed WGS IRA Work Plan	1 day	Fri 10/24/03	Fri 10/24/03
9	WGS IRA Work Plan implementation	23 days	Mon 10/27/03	Wed 11/26/03
10	Development of Decision Procedure Document as a supplement to the Draft Detailed WGS IRA Work Plan	25 days	Mon 10/13/03	Fri 11/14/03
11	MDEQ review of Draft Detailed WGS IRA Work Plan (including Decision Procedure Document)	45 days	Mon 11/17/03	Fri 1/16/04
12	Revision of Detailed WGS IRA Work Plan based on MDEQ input	5 days	Mon 1/19/04	Fri 1/23/04
13	MDEQ review of Detailed WGS IRA Work Plan	19 days	Mon 1/26/04	Thu 2/19/04
14	Approval of Detailed WGS IRA Work Plan	1 day	Fri 2/20/04	Fri 2/20/04
15	Development of Draft WGS Report	26 days	Fri 1/23/04	Fri 2/27/04
16	MDEQ review of Draft WGS Report	23 days	Mon 3/1/04	Wed 3/31/04
17	Revision of Draft WGS Report based on MDEQ review	11 days	Thu 4/1/04	Thu 4/15/04
18	MDEQ final review of WGS Report	11 days	Fri 4/16/04	Fri 4/30/04
19	Issue WGS Report	1 day	Mon 5/3/04	Mon 5/3/04



Project: WGS Timeline
Date: Mon 10/20/03

Task	Summary	Rolled Up Progress	Project Summary
Progress	Rolled Up Task	Split	Group By Summary
Milestone	Rolled Up Milestone	External Tasks	

STATE OF MICHIGAN
DEPARTMENT OF ENVIRONMENTAL QUALITY
LANSING

JENNIFER M. GRANHOLM
GOVERNOR

STEVEN E. CHESTER
DIRECTOR

October 21, 2003

Ms. Susan Carrington
VP and Executive Director of Michigan Dioxin Initiative
The Dow Chemical Company
47 Building
Midland, MI 48667

Dear Ms. Carrington:

SUBJECT: Work Scope for the Interim Response Activity of Evaluating Wild Game Taken From the Tittabawassee River Floodplain for Human Consumption; The Dow Chemical Company (Dow), Midland; MID 000 724 724

Staff of the Department of Environmental Quality (DEQ), Waste and Hazardous Materials Division (WHMD), has reviewed the Work Scope for the Interim Response Activity (IRA) of Evaluating Wild Game Taken from the Tittabawassee River Floodplain, submitted by e-mail on October 20, 2003. This document was submitted in accordance with Condition XI.B.3. of the hazardous waste facility operating license issued to Dow on June 12, 2003.

The purpose of this IRA is to determine if human consumption of wild game taken from dioxin- and furan-contaminated areas of the Tittabawassee River flood plain is a human health exposure pathway that requires immediate mitigation.

The above referenced Work Scope, enclosed in this letter, is approved subject to the stipulations for approval listed below:

1. The anticipated schedule for the collection of the animals shall be provided to this office so that staffs of the DEQ, Department of Community Health, and Department of Natural Resources have the option of conducting oversight of sampling activities. The work plan must also contain provisions for providing the DEQ with splits of the samples for audit purposes.

2. The percent moisture and lipid content of each sample shall be included in the report (in addition to reporting the data on a wet weight and lipid normalized basis) in order to provide maximum flexibility for using the data in the assessment of human health risk.

3. Elements 7 and 8 of Figure 1 indicate that the DEQ will provide review and conceptual approval of the Draft Detailed Wild Game Study work plan within two days of receipt of the work plan. Because of the need to coordinate this review with multiple agencies, a longer time frame may be necessary. The DEQ, however, will make every effort to work with Dow to achieve conceptual approval of the sampling and analysis components of the draft work plan in as rapid a manner as possible in order to allow sampling to be completed prior to the beginning of firearm deer season.

The draft detailed IRA Work Plan shall be submitted to the DEQ by October 23, 2003, the date indicated in the Work Scope schedule.

Contact me be email at taylorab@michigan.gov or at the below telephone number if you have any questions or concerns regarding this approval.

Sincerely,

Allan B. Taylor

Allan B. Taylor, Senior Geologist
Hazardous Waste and Radiological Protection Section
Waste and Hazardous Materials Division
517-335-4799

Enclosure

cc: Mr. John Phillips, Dow
Dr. Lisa Williams, U.S. Fish and Wildlife Service
Mr. Dan O'Brien, Department of Natural Resources
Mr. George Bruchmann, DEQ
Ms. Brenda Brouillet, DEQ - Saginaw Bay
Ms. Sarah Hession, DEQ
Ms. Liane Shekter Smith, DEQ/Corrective Action File
Mr. Steve Buda, DEQ
Ms. De Montgomery/Ms. Ginny Himich, DEQ
Mr. Terry Walkington/Ms. Trisha Peters, DEQ - Saginaw Bay
Dr. Deb MacKenzie-Taylor, DEQ
Ms. Cheryl Howe, DEQ
Mr. Al Taylor, DEQ

Appendix G. MDEQ limited approval of wild game sampling

STATE OF MICHIGAN
DEPARTMENT OF ENVIRONMENTAL QUALITY
LANSING

JENNIFER M. GRANHOLM
GOVERNOR

STEVEN E. CHESTER
DIRECTOR

November 7, 2003

Ms. Susan Carrington
VP and Executive Director of Michigan Dioxin Initiative
The Dow Chemical Company
47 Building
Midland, MI 48667

Dear Ms. Carrington:

SUBJECT: Limited Approval of Sampling Sections of Draft Wild Game Sampling Work Plan for the Tittabawassee River Floodplain Near Midland, Michigan and Transmittal of Technical Review Comments; The Dow Chemical Company (Dow), Midland; MID 000 724 724

Staff of the Michigan Department of Environmental Quality (MDEQ), Waste and Hazardous Materials Division (WHMD), in conjunction with staff of the Michigan Department of Natural Resources (MDNR) and the United States Fish and Wildlife Service (USFWS), has reviewed the Draft Wild Game Sampling Work Plan for the Tittabawassee River Floodplain Near Midland, Michigan (Work Plan), that was submitted on October 23, 2003. This Work Plan was submitted in accordance with Condition XI.B.3. of the hazardous waste facility operating license issued to Dow on June 12, 2003.

At the request of the MDEQ, plat maps showing the proposed wild game sampling locations were submitted to this office on November 2, 2003. In follow up, a field inspection of the proposed sampling locations adjacent to Smith's Crossing and Imerman Park was conducted on November 6, 2003. Based on the results of this field inspection it was determined that at the site adjacent to Imerman Park, the collection of animals should be limited to the lower field and woods adjacent to the Tittabawassee River. As discussed with Dr. Alan Blankenship of ENTRIX, Inc., on November 6, 2003, the upper portions of the proposed site are not likely to contain elevated levels of dioxins and furans and are therefore to be avoided in order to increase the probability of collecting animals that reside in contaminated portions of the floodplain. During the field inspection, Dr. Matthew Zwiernik of Michigan State University (MSU) indicated that preliminary soil sampling results from the site adjacent to Smith's Crossing contained dioxin and furan total toxic equivalence concentrations in excess of 1000 ppt. The final data must be provided in the IRA report.

The cover letter transmitting the draft Work Plan to the MDEQ requested conceptual approval so that wild game sampling can occur upon receipt of the MDNR scientific collector's permit. It is the MDEQ's understanding that the MDNR permit was recently issued. Approval to proceed with the wild game sampling sections of the Work Plan (Sections 2.1 - 2.8.3 and 2.11 - 2.12 and Standard Operating Procedures 214, 229, 230, 231, 401, and 402) is granted, provided this sampling is consistent with the enclosed technical review comments. It is not possible to proceed with conceptual review and approval of the remaining portions of the Work Plan because key sections of the Work Plan such as the Decision Document and the Quality Assurance Project Plan have not yet been submitted.

As indicated in the October 21, 2003, approval letter for the Work Scope for the Interim Response Activity (IRA) of Evaluating Wild Game Taken From the Tittabawassee River Floodplain for Human Consumption (Work Scope), the purpose of this IRA is to determine if human consumption of wild game taken from dioxin- and furan-contaminated areas of the Tittabawassee River flood plain is a human health exposure pathway that requires immediate mitigation. Therefore, when the Work Plan is resubmitted to address the enclosed technical review comments, the title should be revised to be consistent with the approved Work Scope to indicate that it is an IRA Work Plan and that the purpose is to evaluate wild game taken for human consumption. Please submit a revised Work Plan for final review and approval by November 21, 2003. If an alternate date for submittal is needed, please submit a written request to Mr. Al Taylor, Hazardous Waste and Radiological Protection Section, WHMD, at 517-335-4799 or by e-mail at taylorab@michigan.gov.

If you have any questions regarding this limited approval or the technical review comments, please contact me by e-mail at howec@michigan.gov or at the phone number below, or you may contact Mr. Taylor.

Sincerely,

Cheryl Howe

Cheryl Howe, Senior Environmental Engineer
Hazardous Waste and Radiological
Protection Section
Waste and Hazardous Materials Division
517-373-9881

Enclosure
cc:

Dr. Alan Blankenship, ENTRIX, Inc.
Mr. John Phillips, Dow
Dr. Lisa Williams, USFWS
Dr. Matthew Zwiernik, MSU
Dr. Daniel O'Brien, MDNR
Mr. George Bruchmann, MDEQ
Ms. Liane Shekter Smith, MDEQ/Corrective Action File
Mr. Steve Buda, MDEQ
Ms. De Montgomery/Ms. Ginny Himich, MDEQ
Mr. Terry Walkington/Ms. Trisha Peters, MDEQ - Saginaw Bay
Ms. Brenda Brouillet, MDEQ - Saginaw Bay
Ms. Sarah Hession, MDEQ
Dr. Deb MacKenzie-Taylor, MDEQ
Mr. Al Taylor, MDEQ